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CONTENTS.

SUMMARY.

This thesis can be divided into six parts.

The introduction reviews the chemistry of macrocyclic acetylenic compounds, with particular emphasis on the fully conjugated monocyclic polyenes (the annulenes) and the dehydroannulenes, an interesting series of compounds, some of which display aromatic characteristics.

Section I deals with the attempted synthesis of 1,2:7,8:13,14-tribenzocyclooctadeca-1,7,13-triene-3,5,9,11,15,17-hexyne, via a u.v. induced free radical coupling reaction on 1,2-bis(β-iodoethynyl)benzene. Although the desired macrocyclic acetylenic hydrocarbon was not obtained, several interesting naphthalene derivatives were isolated.

Section II deals with the synthesis of the hydrocarbon 1,2-bis-(β-phenylethynyl)benzene and the attempted synthesis of 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne. The synthesis of the latter compound was not completely successful, but the thesis reveals a line of approach which could be successful.

Section III deals with an interesting series of macrocycles, and discusses in detail the i.r. and u.v. spectral characteristics of an interesting series of related diphenylacetylene, stilbene (cis- and trans-) and dibenzyl hydrocarbons, mono-ols and diols.

Section IV is concerned with the coupling of ethynyl compounds under high-dilution conditions. Octa-1,7-diyne was coupled in cupric acetate/pyridine/methanol at various concentrations, and it was found that the ratio of the cyclic dimer to the cyclic trimer increased as

the initial concentration of the diyne decreased.

Section V deals with the hydration of acetylenic compounds. Undeca-1,7-diyne was hydrated under different conditions, and it was found that the two expected diketones, undecane-2,7-dione and undeca-2,8-dione, were always formed in the same ratio, although the former predominated to an unexpected degree. A brief investigation into the hydration of acetylenic compounds using ruthenium trichloride in hydrochloric acid has also been carried out.

INTRODUCTION : MACROCYCLIC ACETYLENIC COMPOUNDS.

The chemistry of macrocyclic acetylenic compounds has excited considerable interest in recent years, and the following introduction comprises a review of the recent work in this field with particular reference to the fully conjugated monocyclic polyenes (the annulenes), derived from macrocyclic acetylenic compounds. (A discussion of some of the earlier results has already been given by Behr[1] and Lardy[2]).

Sondheimer and his co-workers have produced an impressive body of work on macrocyclic acetylenic compounds and on the annulenes derived from them[3-37]. Since Lardy[2] has already reviewed the syntheses of these annulenes, only a brief outline of the synthesis of one of them, [18]annulene(1), will be given here. The properties of the annulenes in general will be discussed, with particular reference to their aromatic character.

Oxidative coupling[38-40] of hexa-1,5-diyne(2) gave, in addition to several other compounds, the cyclic trimer(3)[8,23], which, on treatment with potassium t-butoxide in t-butanol, was converted into 5,11,17-tridehydro[18]annulene(4). Subsequent partial hydrogenation of (4), using the Lindlar catalyst[41], gave[18]annulene(1)[11]. Using the above procedure, and slight variations of it, Sondheimer has synthesised the parent [14]-[17], [16]-[26], [20]-[21,22,27], [24]-[13] and [30]annulenes[15,21,27] (8, 13, 19, 22 or 23, and 25 respectively) as well as [18]annulene(1) itself. In addition, the dehydroannulenes (5^{28}, 6^{32}, 10^{17}, 12^{31}, 14^{26}, 15^{26}, 16^{26}, $20^{22,27}$, 21^{22}, $24^{13,23}$,

26[14,27], 27[14,23] and 28[23]) have been synthesised. A hexamethyl[18]-annulene(17)[30] and the dehydroannulene precursor (18)[30], have also been prepared in this way.

Two derivatives of [10]annulene have been prepared, 1,6-oxido-[10]annulene(29) by Sondheimer and Shani[35], and 1,6-methano[10]annulene(30) by Vogel and Roth[42].

The main interest in the annulenes arises from the question of whether or not monocyclic hydrocarbons formally made up of alternating single and double bonds will show so-called "aromatic" behaviour. The best known example of this type of compound is, of course, benzene(31), ([6]annulene), which has typical aromatic properties, i.e., benzene is planar and does not consist of distinct single and double bonds, but all the carbon-carbon bonds are the same length, and chemically benzene undergoes substitution reactions, rather than the addition reactions which are characteristic of olefins. Speculation was rife as to whether or not the higher vinylogues of benzene would show similar properties. Accordingly, cyclooctatetraene(32), ([8]annulene), was prepared[43], and shown to have no aromatic properties, i.e., the molecule is non-planar, the alternate bonds are of unequal length, and chemically cyclooctatetraene behaves like a normal conjugated polyene.

Later theoretical work[44-46] predicted that annulenes would exhibit aromatic properties if they contained a closed shell of $(4n+2)\pi$-electrons[44], (Hückel's rule), and were reasonably planar[47,48].

In addition, the theory predicts that for the lower members of the $(4n+2)\pi$-electron series, the carbon-carbon bonds will be equal in length, but when n is large, the carbon-carbon bonds will be alternately long and short. In the 4n π-electron series, the theory predicts that the bonds will be alternate for the whole series. Therefore in addition to requiring $(4n+2)\pi$-electrons and being reasonably planar, an annulene will only be aromatic if the ring-size is less than that for which Longuet-Higgins and Salem[45,49] have predicted the occurrence of bond-alternation; unfortunately, the exact value of this limiting ring-size is uncertain.

A manifestation of all the carbon-carbon bonds being the same length, is a large stabilisation energy, whereas, if the carbon-carbon bonds are alternate, a small stabilisation energy is expected; e.g., the stabilisation energy (resonance energy) of benzene is 36 K.Cal./mole, (equal bonds), whereas that of cyclooctatetraene (alternate bonds) is only 4.8 K.Cal./mole. Davies[50] has calculated that the stabilisation energy of [18]annulene will be 103 K.Cal./mole if the molecule is reasonably planar and the bond lengths are equal, whereas, Coulson and Golebiewski[48] have calculated that for a non-planar structure for [18]annulene, in which the steric interactions are at a minimum, the loss in stabilisation energy of [18]annulene would be 70 K.Cal./mole. An X-ray analysis of [18]annulene has now been carried out[32], and, in fact, the molecule is almost planar. The "cis"-type bonds are 1.419 ± 0.004 A^{o} long, and the two "trans"-type

bonds between each "cis"-bond are 1.382±0.003A° in length. The difference, 0.04A°, is appreciable, and cannot readily be explained, but it is much less than in cyclooctatetraene (0.13A°), and certainly precludes appreciable bond-alternation. The heat of combustion of [18]annulene has also been measured, and its heat of formation calculated[34]. The results indicate a stabilisation energy for [18]annulene of 100±6 K.Cal./mole, indicating that [18]annulene is aromatic, and therefore the ring-size must be less than that for which bond-alternation has been predicted[45,49].

It should be pointed out that Hückel's rule decreases in significance with increasing ring-size. The simple theory, on which the rule is based, requires that the delocalisation energies (per π-electron) of (4n+2) and 4n π-electron systems, should approach the same limit as n tends to infinity. However, the legitimacy of the Hückel theory for 4n π-electron systems has been questioned, and it is probable that these systems are indeed inherently less delocalised than the (4n+2)π-electron systems.

Several dehydroannulenes are also discussed in this section, and although Hückel's rule was not formulated for the dehydroannulenes, considerations of the theory suggest that the rule should still be applicable, though of diminished significance[29]. Furthermore, the presence of the carbon-carbon triple bonds will produce bond-alternation, with a subsequent lowering in the degree of aromaticity. In the event, dehydroannulenes obeying Hückel's rule were found to be

aromatic, while those which did not obey it, were not, as will be seen later.

Although there has been no generally accepted definition of aromaticity, a compound is considered to be aromatic if there is a measurable degree of cyclic delocalisation of a π-electron system in the ground state of the molecule[29,51]. As already discussed, this will result in a lower energy content than would be predicted from classical considerations, in carbon-carbon bonds intermediate in length between those usual for single and double bonds, as well as in the ability of the π-electron system to sustain a magnetically-induced current[51]. This last property is associated with a secondary magnetic field which will increase the magnetic susceptibility and diamagnetic anisotropy of the molecule[52], and contribute to the chemical shifts of aromatic protons[53], the latter being measurable by nuclear (proton) magnetic resonance spectroscopy (n.m.r.). In the general case of the macrocycles, aromatic protons may be situated either inside or outside the ring; the former protons will be strongly shielded by the secondary magnetic field, whereas the latter will be deshielded (Fig.1). Sondheimer and his colleagues thus determined the n.m.r. spectra of some of the macrocycles, since those which were "aromatic" in the sense of sustaining a ring current, should show absorption at unusually high fields due to the inner protons, as well as at unusually low fields due to

the outer protons. τ-values were used throughout[54].

A brief summary of the results expected from the theory, together with the results obtained by n.m.r., is given in Table 1. A detailed description of the n.m.r. spectra recorded, together with some other properties, now follows.

[3]Annulene and [8]annulene.

The first two known members of the series, [3]annulene and [8]annulene [i.e., benzene(31) and cyclooctatetraene(32), respectively] are well known. The protons in benzene absorb at 2.74τ, whereas those in cyclooctatetraene absorb at 4.31τ. The olefinic protons in cyclooctatriene absorb at 4.26τ, showing that in cyclooctatetraene no ring current exists, whereas benzene, which absorbs at lower field, does exhibit a ring current.

[10]Annulene.

The next member of the series, [10]annulene(33), has not yet been prepared, but although it has $(4n+2)\pi$-electrons (n=2), Mislow[55] predicts that it will not be aromatic, since it cannot be planar due to steric interaction of the 1,6 hydrogens. However, this strain is alleviated in the two known derivatives, 1,6-oxido[10]annulene(29) and 1,6-methano[10]annulene(30), and, in fact, they are both aromatic in character; e.g., 1,6-oxido[10]-annulene undergoes electrophilic substitution reactions[35], and the protons absorb at low field (2.23-2.81τ) in the n.m.r., and demonstrate the existence of a ring current.

[12]Annulene.

[12]Annulene itself has not yet been prepared[32], but two bisdehydro[12]annulenes(5 and 6) have been prepared by Sondheimer and his colleagues, and the n.m.r. spectra recorded[32].

The bisdehydro[12]annulene of structure (6) has one trans-double bond and three cis-double bonds. The configuration is fully in accord with that shown (6), existing in a non-planar conformation with the trans-double bond perpendicular to the plane of the ring. This causes the protons marked H^1,H^2,H^3 and H^4 on one side of the molecule to be equivalent to the corresponding ones on the other side. The n.m.r. spectrum consists of a quartet at -0.90τ(two H^1 protons), an octet at 4.97τ(two H^2 protons), a band at 5.47τ(two H^4 protons) and a doublet at 5.82τ(two H^3 protons). The spectrum gives no indication of a ring current.

The other bisdehydro[12]annulene(5), has only one band at 5.58τ, which is assigned to all eight protons of the molecule. This compound is presumably not planar, and possesses two different types of protons, which are assumed, not unreasonably, to merge into one band, due to their similar chemical shifts. The only other structure which could reasonably be assumed for this isomer, (7), is discounted since it is unlikely that this compound would show only one band in its n.m.r. spectrum. Once again there is no sign of any ring current.

[14]Annulene.

In the [14]annulene series,a great deal of work has been done by Sondheimer's group, and three very interesting compounds have been made (8,10 and 12). Treatment of the cyclic compound (9) with mild base gave rise to two different conjugated macrocycles, thought at first to be different isomers of monodehydro[14]annulene. One of them was shown to have the structure (10) from its n.m.r. spectrum, which consists of a complex band at low field, (1.2-2.7τ, ten outer protons) and a double doublet at high field, (10.70τ, two inner protons). The ratio of the two bands is almost exactly 5:1, a fact which rules out the alternative structure (11), which would have two bands in the ratio of 3:1. The spectrum shows the existence of a ring current.

The second crystalline compound obtained from base treatment of (9), thought at first to be an isomer of monodehydro[14]annulene, surprisingly turns out to be 1,8-bisdehydro[14]annulene(12), a very remarkable compound containing two hydrogen atoms less than expected. This is an unusual structure (12) in view of the fact that no conventional formula made up of conjugated double and triple bonds can be written for it, since there is an odd number of carbon atoms on either side of the two formal triple bonds. The molecule should be able to exist in a planar configuration, and has been shown by X-ray measurements[56] to be planar. The n.m.r. spectrum shows a quartet at 0.45τ (four outer H^2 protons), a

doublet at 1.57τ(four outer H^1 protons) and a symmetrical triplet at 15.54τ(two inner H^3 protons). This clearly indicates the existence of a strong ring current. Electrophilic substitution reactions have been carried out on this compound, and these take place at the carbon atom adjacent to the triple bond, H^1 being replaced by SO_3CH_3 , NO_2 , and $COCH_3$. It should be pointed out that monodehydro-[14]annulene(10) can also be substituted with the same substituent groups, although the actual position of substitution is not known, whereas [14]annulene(8) itself (see below) does not undergo electrophilic substitution reactions.

[14]annulene(8) has been postulated by Mislow[55] to be non-coplanar due to steric interactions of the hydrogen atoms at C_1 , C_4 , C_8 , and C_{11} , and hence, although it complies with Hückel's rule (n= 3), it should be non-aromatic. That [14]annulene has the configuration shown (8) was proved by the X-ray crystallographic determination carried out by Bregman[57]. The analysis confirms the configuration (8), but the results do not as yet provide any quantitative information regarding the degree of planarity of the molecule. The n.m.r. spectrum of [14]annulene consists of two bands, a weak one at 3.93τ and a stronger one at 4.42τ. Sondheimer had at first assumed that this weak band was due to a decomposition product of [14]annulene, formed during transport of the sample from Israel to England for the n.m.r. determination. However, it was shown later, that the n.m.r. spectrum of freshly prepared solutions,

still showed both peaks, and that the ratio was roughly 1:6(3.93:4.42). Accordingly, Sondheimer postulated[32] that due to the overcrowding of the inner protons in a planar molecule, the substance existed in a non-planar conformation derived from the planar structure (8), by moving one of the H^1 protons upwards and the other downwards, while the inner protons H^2, stayed inside the ring. These two inner protons (H^2) were then assigned to the 3.93τ band, the 4.42τ band being assigned to the twelve other protons of the molecule. The absence of a ring current in the n.m.r. spectrum indicated that the compound was apparently non-aromatic. However, much later[36], Sondheimer demonstrated that this interpretation of the two bands in the n.m.r. spectrum was incorrect. Thin layer chromatography (t.l.c.) of [14]annulene on silica, had shown only one spot as expected, but t.l.c. on silica which had been impregnated with silver nitrate showed two unequal neighbouring spots, the slower moving one being present in the larger amount. On rapid extraction with ether and rechromatography, the two spots were hardly changed. However, equilibrium of the two conformers was fairly rapid, and rechromatography of an ether solution of either spot after storage for thirty minutes produced two spots, identical with the original mixture. Crystalline [14]annulene consists almost entirely of the slower moving conformer, for immediate examination of freshly prepared solutions gave essentially only the 4.42τ peak. After thirty

minutes, the n.m.r. spectra showed the usual two peaks of the equilibrium mixture. That the equilibrium is temperature-dependent was demonstrated by n.m.r., the 3.93τ peak increasing in proportion with temperature. A likely explanation for the isomerism is that the conformers have structures represented by (35), with the hydrogens at 1 and 2 above those at 3 and 4, and (36) with the hydrogens at 1 and 3 above those at 2 and 4. The room-temperature X-ray study[57] of crystalline [14]annulene indicates that the molecules are centrosymmetric, hence the isomer which gives rise to the 4.42τ peak is presumably (35). Even later[37], the n.m.r. spectrum of [14]annulene was found to be temperature-dependent, and on cooling, the 4.42τ band broadened until at -30° it could no longer be recognised. At -40°, a new very broad band at ~2.7τ became apparent. This band became progressively less broad on further cooling, and a second new band at ~10τ was found to be associated with it. At -60°, the spectrum consisted of broad peaks at 2.4τ and 10.0τ, as well as the 3.93τ peak which had broadened slightly. The 2.4τ band is assigned to the ten outer protons, and the 10.0τ band to the four inner protons. The areas of the bands were approximately in the ratio 5:2. Hence the low temperature n.m.r. spectrum of [14]annulene is typical of an aromatic substance, showing the presence of a ring current which shields the inner protons and deshields the outer protons.

[16]Annulene.

Now let us deal with the [16]annulene series. The n.m.r. spectrum of [16]annulene(13) shows only one band at 3.27τ, this position being close to that observed for the olefinic protons of linear conjugated polyenes. No ring current is observed, but this can no longer be taken as a criterion for lack of aromaticity, unless low temperature n.m.r. spectral studies show no change. The 3.27τ band could be the average of the inner and outer protons, although this is unlikely in this case. This experiment has, unfortunately, not yet been carried out for [16]annulene.

The n.m.r. spectrum of one of the bisdehydro[16]annulenes confirms the structure shown (13). It consists of a quartet centred at 2.25τ (four H^1 protons), an octet at 4.35τ (four H^2 protons) and a doublet at 4.93τ (four H^3 protons). Again no ring current is in evidence.

[18]Annulene.

The case of [18]annulene(1) is perhaps the most interesting. It was, in fact, the first annulene after benzene and cyclooctatetraene to be prepared, and its properties have been well studied, (see above). The n.m.r. spectrum, shows the existence of a ring current. The spectrum consists of two broad bands at 1.1τ (outer protons) and 11.8τ (inner protons) in the ratio of 2:1. As in the case of [14]annulene, low temperature n.m.r. studies have now been carried out[37], and, in fact, the two broad bands become sharper and

show fine structure as the solution is cooled. The separation also is increased, until at -60°, there is a quartet-like band at 0.72τ and a complex band centred at 12.90τ. The ratio remains unchanged at 2:1. This is indicative of an increased ring current, presumably due to increased coplanarity, as thermal disturbances are reduced. Heating a solution of [18]annulene causes the bands at 1.1τ and 11.8τ to broaden, until at 40° they are no longer recognisable. At 60°, a broad new peak at ~4.6τ appears, which sharpens as the temperature is increased, until at 110°, the spectrum consists of a relatively sharp singlet at 4.55τ. The changes with temperature observed for the spectra of both [14]annulene and [18]annulene were found to be reversible. It appears that the n.m.r. spectra of [14]annulene and [18]annulene are similar, except that the transition from the two-band spectrum (aromatic) to the single-band spectrum occurs at lower temperatures in the case of [14]annulene. The most likely explanation for the occurrance of the singlet at higher temperatures, is that the protons change position so rapidly at higher temperatures, that an average value results for the band location. In fact, the position for the singlet is, in each case, in good agreement with that calculated by taking the weighed average of the outer and inner band locations. Both compounds therefore presumably possess a ring current, even in the temperature range in which the n.m.r. spectrum shows only a single peak.

Tridehydro[18]annulene(4) also shows the presence of a ring current in the n.m.r. The spectrum consists of a complex multiplet at 1.7-3.1τ (outer protons) and a double doublet at 8.26τ (inner protons). X-ray measurements[58] indicate that the molecule is planar and has the structure shown (4).

The hexamethyl-tridehydro[18]annulene(18), due to solubility problems, shows only the methyl protons in the n.m.r., and these absorb at 7.40τ. This is lower than the normal value for the angular methyl groups in the carotenoids and their acetylenic analogues[59] (7.95-8.15τ), and, in fact, the methyl protons must be deshielded due to a ring current.

Note that the porphyrins, if written as in structure (37), are similar to [18]annulene(1), and, in fact, the imino protons of this type of molecule occur at very high field (~14τ), whereas the peripheral protons occur at low fields (0-1τ), indicating the presence of a ring current[60-62].

[20]Annulene.

Although [20]annulene(19) has been prepared, Sondheimer has not yet discussed the n.m.r. spectrum.

[24]Annulene.

The next member of the series which has been prepared is [24]annulene(22). The n.m.r. spectrum of [24]annulene consists of a single band at 3.16τ, and no ring current is in evidence, although low temperature studies will have to be carried out, to

ensure that this band is not an average of any other bands.

The n.m.r. spectrum of tetradehydro[24]annulene(24), consists of a double doublet at 1.80τ (inner protons), and a complex multiplet at 3.6-4.7τ (outer protons). That the assignments are correct follows from the relative intensities of the two bands. Again no ring current is in evidence.

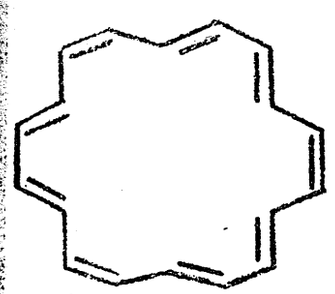
[30]Annulene.

The largest member of the series which has been prepared to date is [30]annulene(25). However this substance is too insoluble to allow the determination of its n.m.r. spectrum. This is unfortunate, since the ring-size may be large enough to produce band-alternation, and this would be reflected in the absence of a ring current in the n.m.r. spectrum.

In conclusion, it would therefore appear that of the fully conjugated cyclic polyenes which have been investigated to date, those which have $(4n+2)\pi$-electrons are aromatic in that they display a ring current in the n.m.r., and those which have $4n$ π-electrons are non-aromatic. However, the $4n$ π-electron compounds require further low-temperature n.m.r. studies to find out whether there is any change in the spectrum, from a one-band to a two-band (aromatic) type, on cooling the solution.

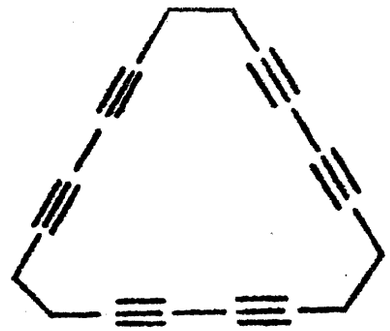
Some other interesting macrocyclic acetylenic compounds which have been prepared in the last few years will now be briefly considered. The highly strained cyclic hydrocarbon (38) was prepared in this department[53], by the oxidative coupling of o-diethynylbenzene(39). Nakagawa and his co-workers[64] have since prepared a similar compound (40), by a similar coupling of (41). In addition, they have successfully dimerised (42) to(43)[65], and (44) to (45)[66,67], and more recently they have made the related hydrocarbons (46)[68] and (47)[69], by oxidative coupling of (48) and (49), respectly.

We in this department have been interested in a series of eight closely related structures (38,50,51,52,53,54,55 and 56), since they should have some striking properties, spectral and otherwise. Three of them (38,53 and 55) have already been prepared[1,2], and this thesis deals mainly with the preparation of another one (56), together with the attempted syntheses of (51) and (52).



[18]annulene
(1)

(2)



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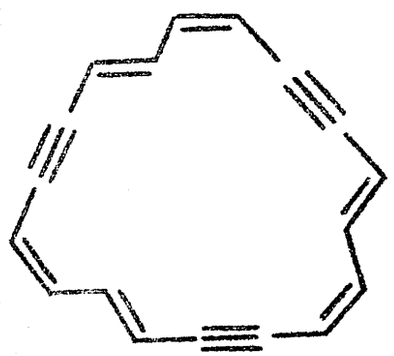

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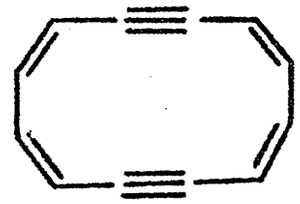

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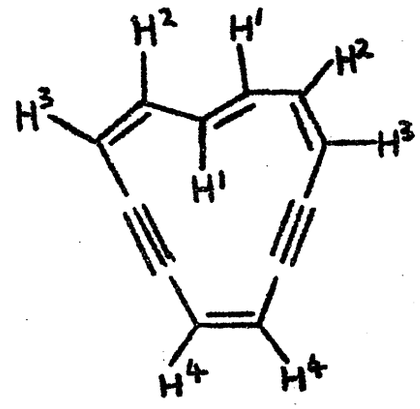

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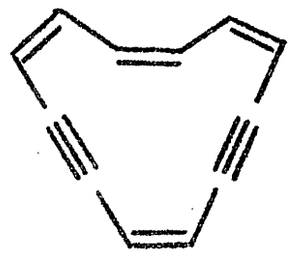

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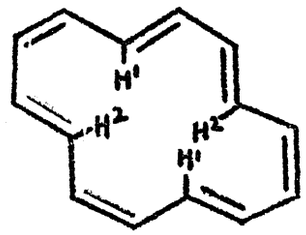
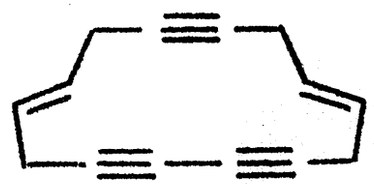


[14]annulene
(8)



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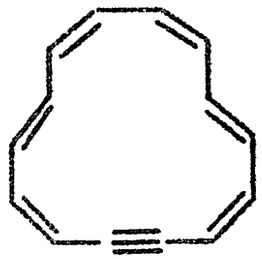

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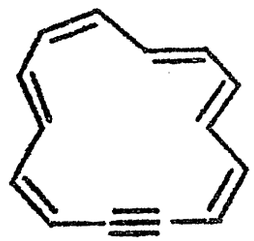

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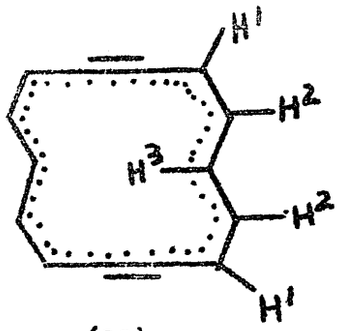

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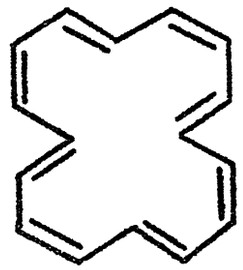

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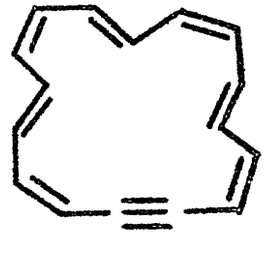

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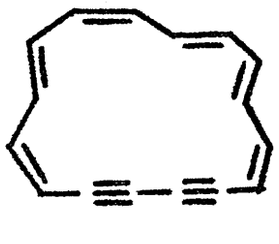

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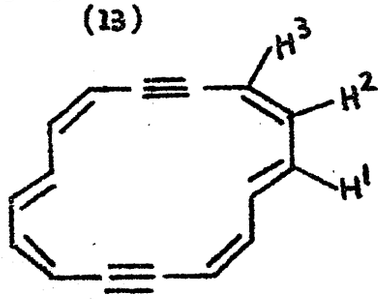

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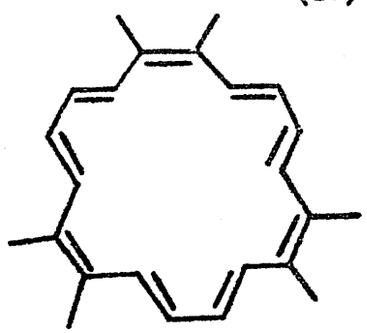

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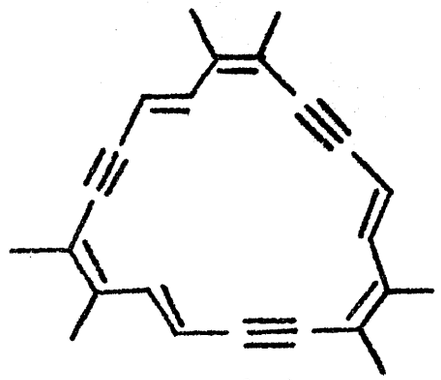

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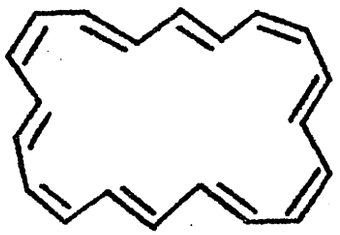

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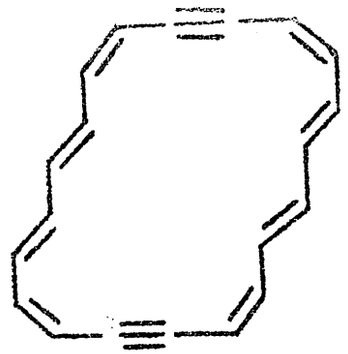

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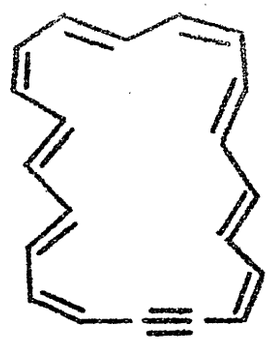

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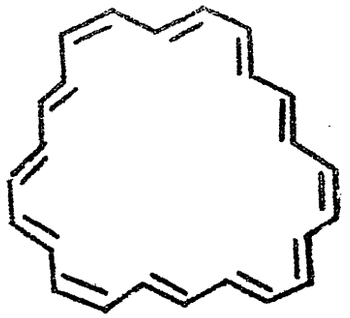

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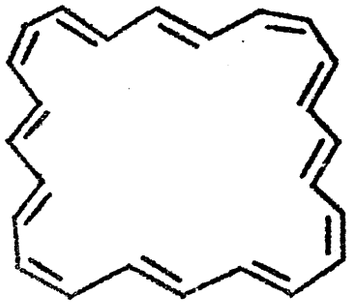

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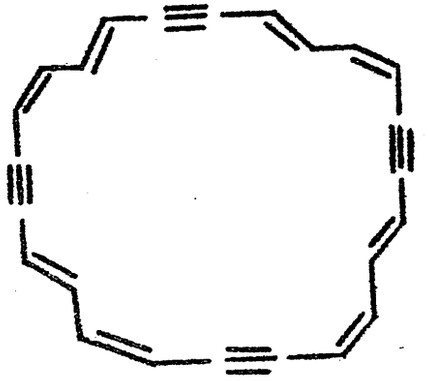

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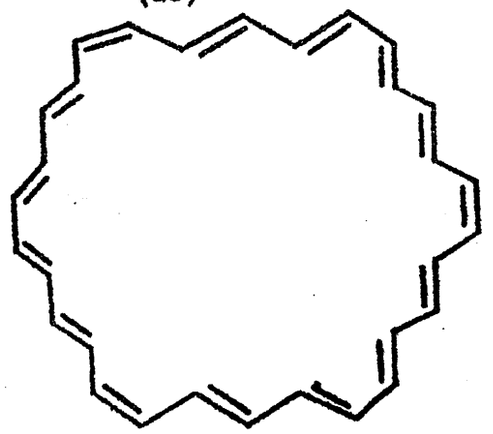

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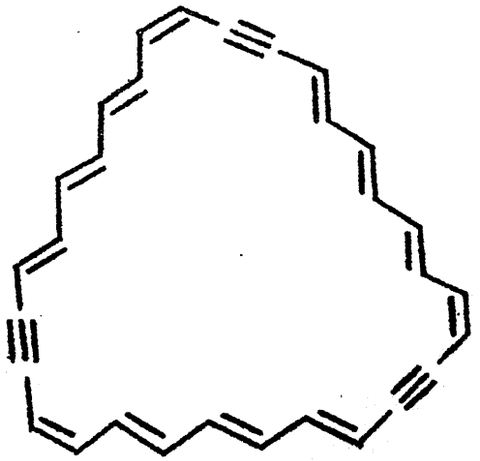

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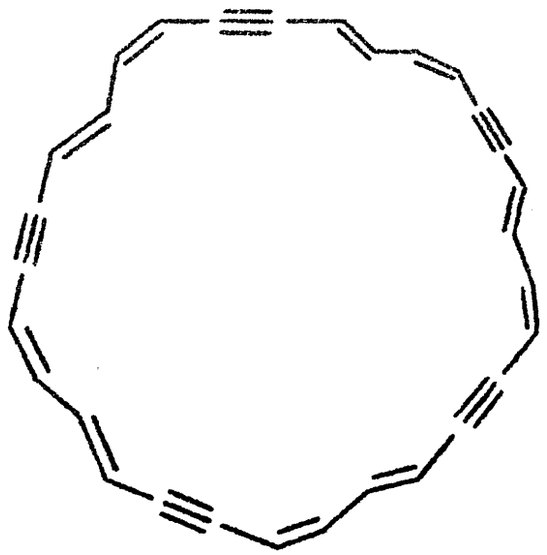

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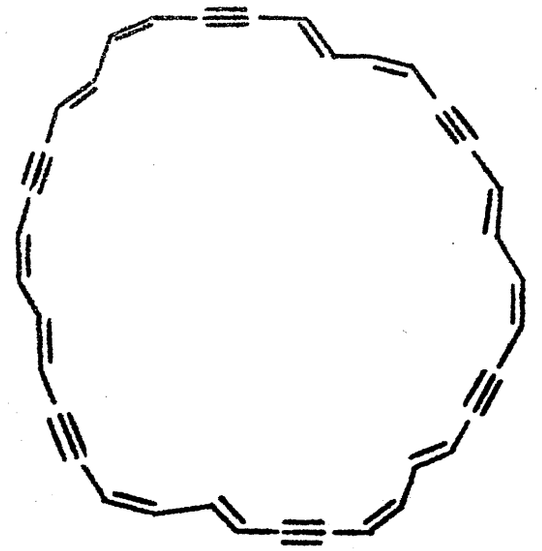

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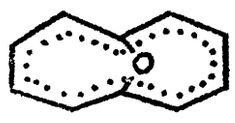

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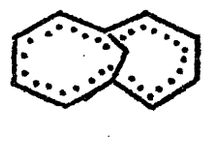

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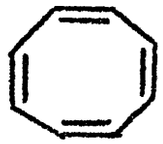

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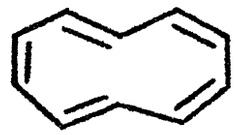

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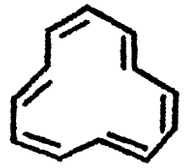

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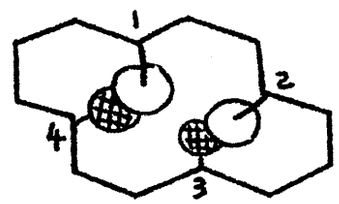

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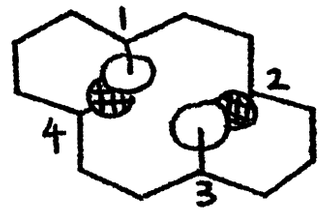

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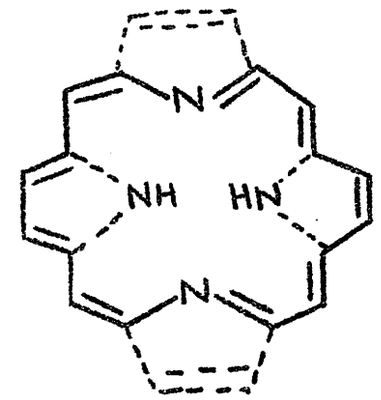

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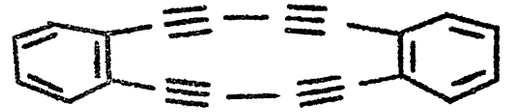

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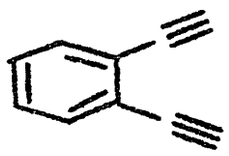

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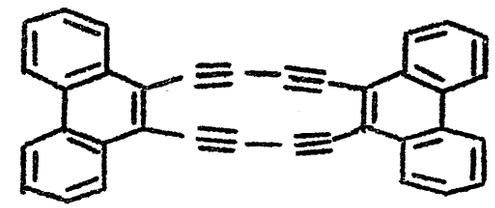

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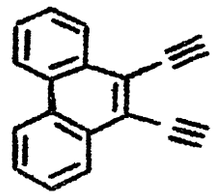

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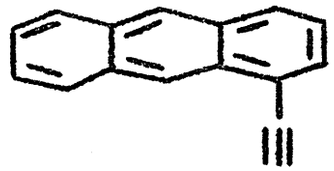

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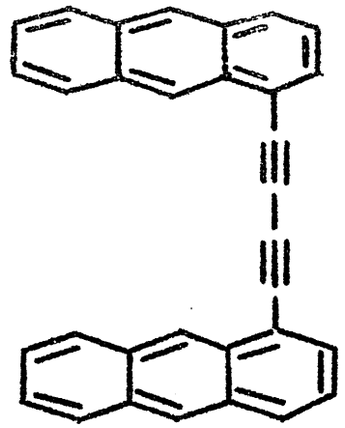

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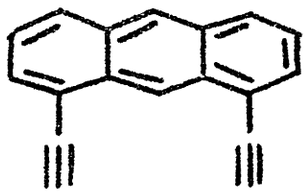

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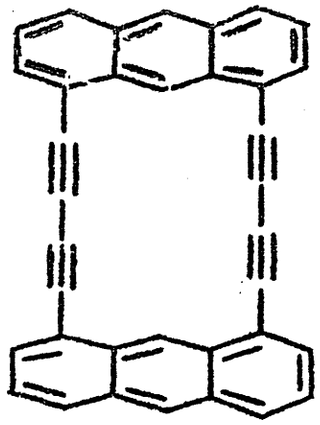

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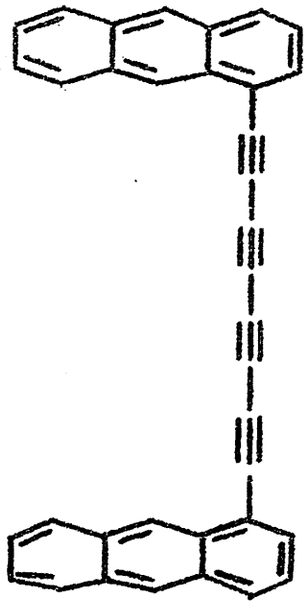

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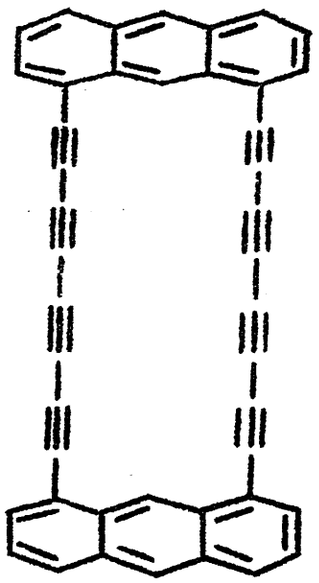

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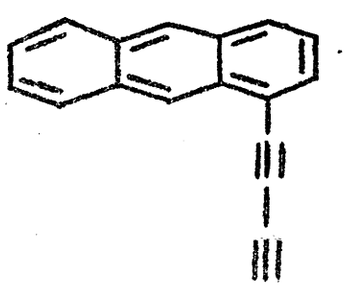

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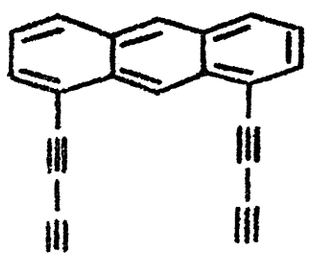

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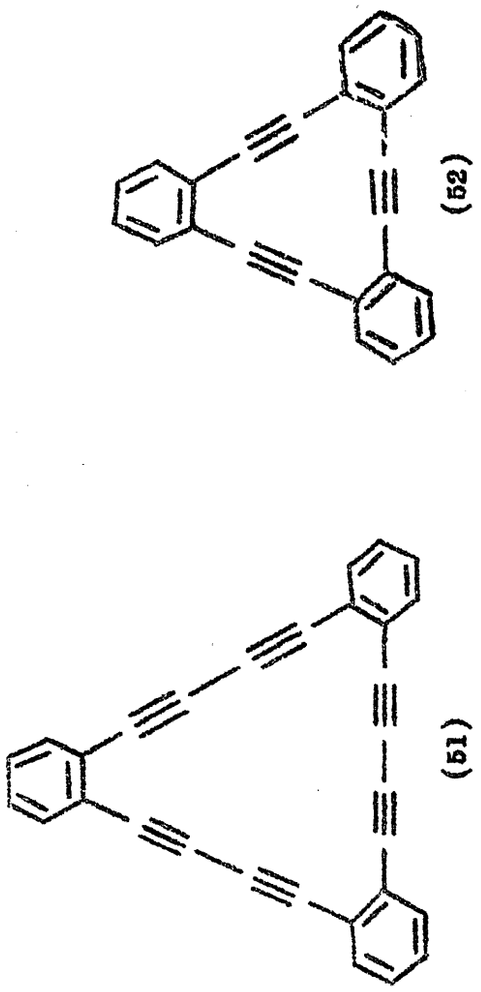

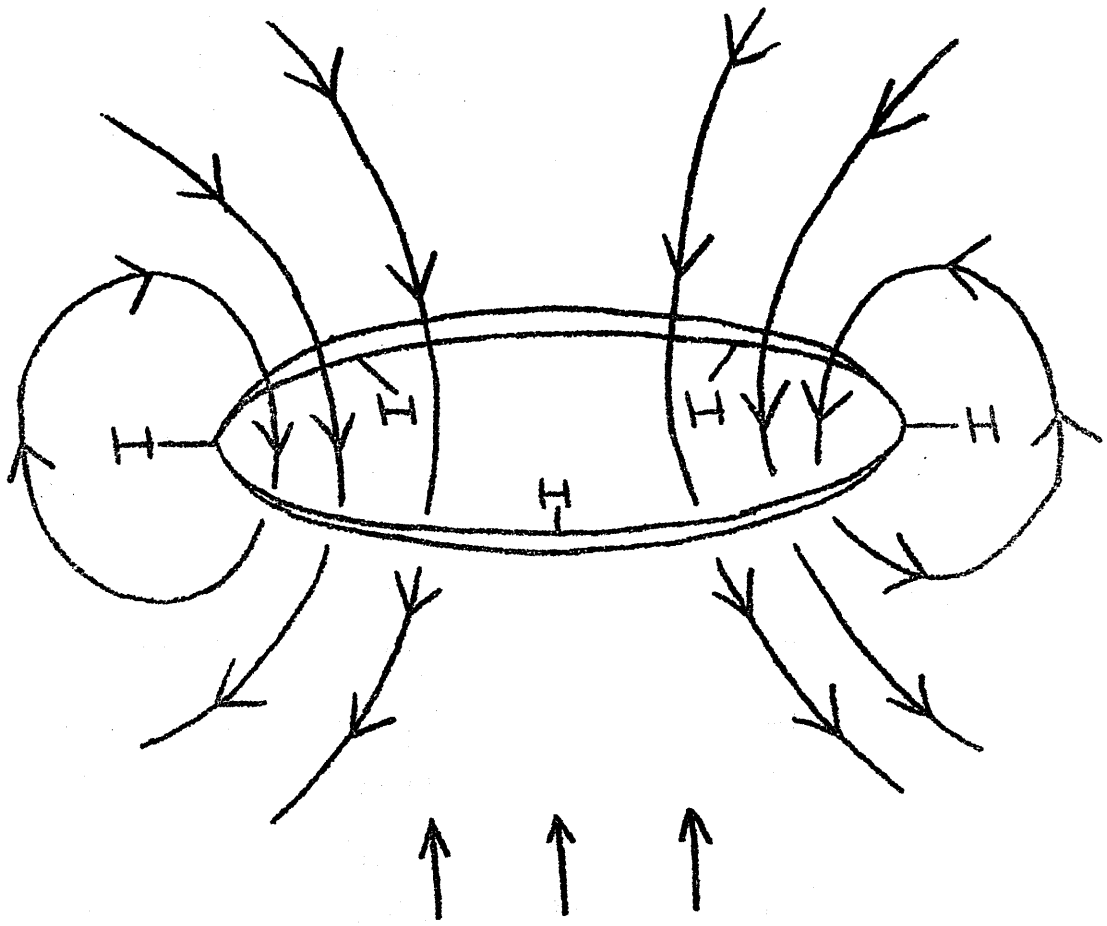

Fig.1.

Shielding of the inner protons, and deshielding of the outer protons, in cyclic compounds capable of sustaining a magnetically induced ring current.

TABLE 1 : THE ANNULENES.

Compound.	Molecular Formula.	Reference.	$(4n+2)\pi$-electrons. Value of n.	n.m.r. τ-values.
Cyclobutadiene	C_4H_4	—	—	—
Benzene(31)	C_6H_6		n=1	2.74τ.
Cyclooctatetraene(32)	C_8H_8	43	—	4.31τ.
[10]Annulene(33)	$C_{10}H_{10}$	—	n=2	—
1,6-Oxido[10]annulene(29)	$C_{10}H_8O$	35	n=2	2.23-2.81τ.
[12]Annulene(34)	$C_{12}H_{12}$	—	—	—
5,11-Bisdehydro-[12]annulene(5)	$C_{12}H_8$	28	—	5.58τ.
7,11-Bisdehydro-[12]annulene(6)	$C_{12}H_8$	32	—	-0.90,4.97, 5.47,5.82τ.
[14]Annulene(8)	$C_{14}H_{14}$	17	n=3	2.4,10.0τ.*
Monodehydro[14]-annulene(10)	$C_{14}H_{12}$	17	n=3	1.2-2.7, 10.70τ.
Bisdehydro[14]-annulene(12)	$C_{14}H_{10}$	31	n=3	0.45,1.57, 15.54τ.
[16]Annulene(13)	$C_{16}H_{16}$	26	—	3.27τ.
7,15-Bisdehydro[16]-annulene(16)	$C_{16}H_{12}$	26	—	2.25,4.35, 4.93τ.
[18]Annulene(1)	$C_{18}H_{18}$	11	n=4	0.72,12.99τ.†
Tridehydro[18]-annulene(4)	$C_{18}H_{12}$	11	n=4	1.7-3.1, 8.26τ.
Hexamethyl[18]annulene(17)	$C_{24}H_{30}$	30	n=4	—
Hexamethyl-tridehydro-[18]annulene(18)	$C_{24}H_{24}$	30	n=4	7.40τ.
[20]Annulene(19)	$C_{20}H_{20}$	21	—	—
[22]Annulene	$C_{22}H_{22}$	—	n=5	—
[24]Annulene(22)	$C_{24}H_{24}$	13	—	3.16τ.
Tetradehydro[24]-annulene(24)	$C_{24}H_{16}$	13	—	1.80,3.6-4.7τ.
[30]Annulene(25)	$C_{30}H_{30}$	15	n=7	—

* low-temperature only.
† low-temperature.

SECTION I

IRRADIATION OF 1-IODO-2-ARYLACETYLENES.

In 1948, Sworski[70] postulated that the triene-triyne (57), should be able to exist in a resonance stabilised cumulene form (58), and so should be a stable compound. This compound might be further stabilised, both sterically and electronically, by a benzo group at each apex (52). A similar argument would presumably apply to a compound containing $\alpha\gamma$-diyne units, (59), which is, in fact, hexadehydro[18]annulene, and this compound, and the tri-benzo-derivative (51), should also be capable of existing in resonance stabilised forms.

Attempts have therefore been made in this department to synthesise (51) and (52). These compounds should be rigid, planar and stable, and a study of the bond lengths and spectral properties would be of considerable interest. There should be some measure of conjugation around the ring, and the availability of the electrons might allow of complexing a metal ion within the molecule. Reactions such as hydration and hydrogenation seem worthy of investigation, due to the possibility of trans-annular reaction, which has been shown to occur in the chemical and catalytic reduction of the related hydrocarbon (38)[1].

The attempted synthesis of (52) is dealt with mainly in Section II of this thesis. The present section is concerned with unsuccessful attempts to synthesise (51), via a u.v. induced free radical reaction, which involves homolytic fission of

carbon-iodine bonds.

Previous attempts to synthesise (51), by oxidative coupling of o-diethynylbenzene(39), surprisingly yielded only the "dimer"* (38), an unusual highly-strained compound. This coupling experiment has been repeated, mainly to obtain a sample of (38) for comparison purposes, but it was also hoped that sensitive techniques, such as thin-layer chromatography (t.l.c.) and mass spectrometry, might reveal a small amount of the trimer (51). The previous coupling[1] had been carried out under high-dilution conditions, and it was felt that coupling under more concentrated conditions would perhaps improve the chances of obtaining the trimer (51), since the ratio of trimer: dimer obtained in the coupling of octa-1,7-diyne(60), was found to decrease on dilution. (See Section IV).

In the event, no compound of structure (51) could be detected after oxidative coupling of o-diethynylbenzene(39). However, the mass spectrum of (38), which had been purified by t.l.c., showed that not only was (38) present, but that there also appeared to be significant amounts of the ene-triyne (61), and the diene-diyne (62 or 63). This is unusual, since the conditions of the coupling

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* While the terms dimer, trimer,... etc., are not strictly accurate, since two hydrogen atoms are removed in each coupling, the terminology is very useful, and has been used throughout.

reaction were considered sufficiently different from the conditions normally exployed[71,72] for the "Straus Reaction", to preclude the possibility of ene-yne coupling.

The properties of this crystalline material (obtained from preparative t.l.c.), were, however, identical to those already reported for (38),and it may be that (38) is so unstable in the electron beam of the mass spectrometer that it gives an abnormally weak parent ion, thereby increasing the relative significance of the molecular ions of (61) and (62 or 63); the latter compounds may, in fact, be present only in very small amounts.

In 1959, Blair, Bryce-Smith and Pengilly[73] reported that photolysis of iodobenzene in iso-propylbenzene gave a mixture of isomeric iso-propylbiphenyls. In 1961, Wolf and Kharasch[74] extended this reaction to a number of substituted iodobenzenes. They carried out the irradiations at room temperature, using essentially one wavelength (2537 Å), which they found produced scission of the carbon-iodine bond, without extensive subsequent reactions of the products or undesired side reactions. In this way they prepared a number of substituted biphenyls in synthetically useful yields, e.g., photolysis of o-iodophenol (64) in benzene gave 2-hydroxybiphenyl (65) in 70% yield.

Later, Kharasch and his co-workers[75,76] further increased the scope of this reaction, irradiating not only substituted iodobenzenes,

but also (66) and (67), which on photolysis in benzene solution gave (68) and (69), respectively. They also reported that photolysis of 1-iodo-2-phenylacetylene(70) in benzene, gave diphenylacetylene(71) in 50% yield, and that similar treatment of (72) gave a 32% yield of (73). At the same time, Kharasch and his co-workers[76] noted that irradiation of iodobenzenes in cyclohexane, methanol or ethanol, gave only the parent hydrocarbon, i.e., the iodine is replaced by a hydrogen atom from the solvent.

Since irradiation of (70) in benzene gives (71), via attack of the free radical (74) on the benzene, then it is reasonable to presume that this free radical (74) could perhaps be induced to self-couple in an inert solvent to give diphenyldiacetylene(75). It was also thought that this irradiation technique, if extended to 1,2-bis(β-iodoethynyl)benzene(76) in benzene could lead to the hydrocarbon (56), the hydrocarbon (51) [or perhaps (38) or (53)] on irradiation of (76) in an inert solvent, and perhaps even (52) on irradiation of (76) in diphenylacetylene(71).

In the event, self-coupling of the radical (74) resulted in diphenyldiacetylene(75), but neither (51) nor (52) was obtained from the irradiation of (76). However, several interesting compounds were obtained. The results are summarised in Table 2, and the relevant details, together with the preparations of the iodo-acetylenes, now follow.

Iodo-acetylenes can be prepared by treating the acetylene with iodine in liquid ammonia[77], but this reaction is generally much smoother, and produces better yields, when carried out on the sodium salt of the acetylene[78]. In this way, phenylacetylene(77) was converted into 1-iodo-2-phenylacetylene(70) in good yield, but this route gave only a small yield of 1,2-bis(β-iodoethynyl)-benzene(76). However, (76) was obtained by treating o-diethynyl-benzene(39), [prepared by potassium t-butoxide/benzene dehydro-bromination of the bromide (78), provided by Lardy[2]], with the complex of morpholine and iodine[79], (79 or 80), in the manner described by Southwick and Kirchner[80] in their preparation of (81) from the ethynyl carbinol (82).

The reported irradiation of 1-iodo-2-phenylacetylene(70) in benzene, to give diphenylacetylene(71), was repeated, and, in fact, (71) was obtained in excellent yield. T.l.c. and u.v. techniques, revealed that direct self-coupling of the radical (74) to give diphenyldiacetylene(75), only took place in very concentrated solutions (1: 5), and even then only to a slight extent (~3%). However, at least three additional compounds were detected, and these were shown to be due to subsequent reaction of (71), since the same three spots on t.l.c. were obtained when (71) was irradiated in either benzene or hexane. Büchi, Perry and Robb[81], have reported that the irradiation of (71) in hexane gives a triphenylazulene (83), a triphenylnaphthalene (84), hexaphenyl-

benzene(85) and octaphenylcubane(86), [now known[82] to be octaphenylcyclooctatetraene(87)]. Again, Bryce-Smith and Lodge[83] have irradiated substituted acetylenes in benzene, and have identified substituted cyclooctatetraenes; thus, (88) on irradiation in benzene gives (89) and (90), presumably via an intermediate valence bond isomer (91). Diphenylacetylene(71) might therefore be expected to produce (92) and (93), rather than the four compounds reported by Büchi and his co-workers[81], but this was not further investigated. When phenylacetylene(77) is irradiated in benzene, (94) and (95) are obtained, as well as the expected phenylcyclooctatetraene(96)[83]. (94) and (95) are formed in the same ratio when phenylacetylene(77) is irradiated in hexane[83].

Returning to the present studies, 1-iodo-2-phenylacetylene(70) was irradiated in carbon tetrachloride and in cyclohexane. These solvents are relatively unreactive and would not be expected to impede self-coupling of the radical (74). In the event, no diphenyldiacetylene(75) was produced in either of these irradiations. A t.l.c. study of the product formed by irradiation in carbon tetrachloride, showed that the starting material (70) had been used up. Instead, a large fluorescent spot, tailing just above the origin was present. This is possibly a compound of type (97), produced by attack of the radical (74) on the solvent. This was not further investigated.

The irradiation in cyclohexane also showed no starting material

on t.l.c., and the i.r. spectrum of the product was virtually identical to that of phenylacetylene(77), which is perhaps to be expected from Kharasch's findings[76] on the irradiation of the substituted iodobenzenes in cyclohexane (see above). However, t.l.c. showed that other spots were present, and an almost identical t.l.c. behaviour was revealed when phenylacetylene(77) itself was irradiated in cyclohexane, showing that these spots were due to subsequent reaction of the phenylacetylene(77) (see above), formed by attack of the radical (74) on the solvent.

Self-coupling of the radical (74) did take place, however, when the iodophenylacetylene(70) was irradiated as a thin liquid film. In addition to unchanged starting material (70) (38%), diphenyldiacetylene(75) was obtained, on chromatography, in moderate yield (27%). T.l.c. also showed that several other spots were present, and these were not formed by subsequent reaction of (75), since (75) was recovered unchanged on irradiation in benzene. These other compounds are presumably formed by attack of the radical (74) on the aromatic ring of another molecule, leading to other structures, possibly of type (98).

The availability of a sample of di-iodoacetylene(99) invited its irradiation in benzene. Diphenylacetylene(71) was detected in the reaction mixture by u.v. and t.l.c., but attempted isolation of (71) by chromatography was unsuccessful. Several other spots were present on t.l.c., but although unchanged starting material

could be detected in the reaction mixture by its characteristic unpleasant odour, no spot was observed on t.l.c. corresponding to 1-iodo-2-phenylacetylene(70), presumably the first-formed product. This seems to indicate that (70) is much more reactive than (99), probably because the radical (74) is more stable than the radical (100).

The irradiation of 1,2-bis(β-iodoethynyl)benzene(76) in benzene was expected to yield the hydrocarbon(56). In the event, (56) was isolated from the reaction mixture (~40% yield), identified by t.l.c., u.v. and i.r. comparison with an authentic sample (Section II), and also by mass spectrometry, (parent ion at 278; $C_{22}H_{14}$ requires M.W. 278). However, five other spots, (mostly all pale yellow in visible light) were observed on t.l.c. of the crude product. The R_F values were large compared to that of (38), and it seemed unlikely that (51), (38) or (53) had been formed. It was felt that these compounds were perhaps formed by subsequent reaction of (56), or perhaps (51), (38) or (53). However, irradiation of (38) in benzene did not produce any corresponding spots, but irradiation of (56) in benzene did produce a spot on t.l.c., corresponding to the one just above that of (56) itself. The fraction corresponding to this spot was later shown, by preparative t.l.c. and mass spectrometry, to be a compound of molecular weight 356, and is thought to have structure (84).

Preparative t.l.c. separated the fractions corresponding to the

four yellow spots, plus a fifth fraction corresponding to the last two closely-running spots.

(i) The first fraction, corresponding to the spot of R_F 0.6, had a u.v. spectrum which was very similar to that of the hydrocarbon(53) (Fig.2), and the i.r. spectrum showed absorption typical of a 1,2-di-substituted aromatic ring. However, the compound ran faster on t.l.c. than (38), and it was thought that structure (51) or (53) was therefore unlikely. The mass spectrum showed a molecular ion at 506, and large ions and metastable ions corresponding to three successives losses of 127 mass units. This would suggest that three iodine atoms were present in the molecule, and the remaining mass, 125, suggests a $C_{10}H_5$ fragment. A possible structure for this compound is tri-iodonaphthalene, and this was confirmed, since hydrogenolysis(5% palladium on charcoal in ethyl acetate) gave naphthalene, (identified by g.l.c. comparison with an authentic sample). This does not indicate the positions of the iodine atoms on the naphthalene nucleus, but it is most likely from the mode of formation that the arrangement is either 1,2,3- or 1,2,4-,(101) or (102), respectively. However, the aromatic substitution pattern in the i.r. spectrum was very similar to that of 1,2,3-trichloronaphthalene, and substantially different from that of 1,2,4-trichloronaphthalene[84], which therefore favours structure (101). Only one tri-iodonaphthalene has so far been reported in the literature [85], and in this compound, the substitution

pattern is not known.

The mass spectrum of this fraction suggested that a compound of molecular weight 380 was also present. $C_{10}H_6I_2$ requires a molecular weight of 380, and this compound is likely to be a di-iodonaphthane [probably (103)].

(ii) The second fraction, corresponding to the spot on t.l.c. of R_F 0.5, was shown by mass spectrometry to be a mixture of two compounds; the minor component had a molecular weight of 632 corresponding to $C_{10}H_4I_4$, structure (104), the other a molecular weight of 456. The i.r. spectrum showed that in addition to a 1,2-di-substituted aromatic ring, a mono-substituted aromatic ring was also present. This, in addition to the mass spectrum, suggests a $C_{10}H_5$ naphthalene nucleus, substituted with two iodine atoms and a C_3H_5 phenyl group ($C_{16}H_{10}I_2$ requires M.W. 456). The structure is probably (105), (see below). Hydrogenolysis should give 1-phenylnaphthalene, and this experiment has been carried out. The u.v. spectrum of the crude hydrogenated product favours the presence of 1-phenylnaphthalene as opposed to the 2-isomer, since their u.v. spectra are markedly different[86,87]. Confirmatory g.l.c. analysis by comparison with authentic samples has yet to be carried out.

(iii) The third fraction again showed 1,2-di- and mono-substituted aromatic absorption in the i.r. spectrum, and the mass spectrum (molecular ion 582, $C_{16}H_9I_3$ requires M.W. 582) suggests structure (106). Again, hydrogenolysis appears to give the expected 1-phenyl-

naphthalene, from a study of the u.v. spectrum of the crude hydrogenated product, and g.l.c. analysis should give confirmatory evidence.

(iv) The fraction corresponding to the spot of R_F 0.3 was shown by mass spectrometry to consist of two compounds, the main parent ion being at 532, [structure (107), $C_{22}H_{14}I_2$ requires M.W. 532] and the other parent ion at 280, [structure (108), $C_{22}H_{16}$ requires M.W. 280].

(v) The last fraction was shown to be mainly (56); i.r., u.v. and t.l.c. identical to an authentic sample (Section II) while mass spectrometry showed a very large parent ion at 278 due to (56), plus a significant parent ion at 356, [structure (84), $C_{28}H_{20}$ requires M.W. 356].

Thus, in addition to the expected hydrocarbon (56), eight substituted naphthalenes appear to have been formed in this reaction, namely,

(i) A di-iodonaphthalene (103),

(ii) A tri-iodonaphthalene(101),

(iii) A tetra-iodonaphthalene(104),

(iv) A diphenylnaphalene(108),

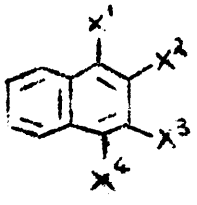
(v) A triphenylnaphthalene(84),

(vi) A phenyl-di-iodonaphthalene(105),

(vii) A diphenyl-di-iodonaphthalene(107),

(viii) A phenyl-tri-iodonaphthalene(106).

If it is assumed that (76) on irradiation in benzene, reacts via a di-radical (109) to give, in addition to the hydrocarbon (56), a naphthalene type skeleton, which then picks up any four radicals at random, then, disregarding individual arrangements of any one type of substituted naphthalene, fifteen possible substituted naphthalenes can be formed, I–XV below.



	X^1	X^2	X^3	X^4	M.W.
I	H	H	H	H	128
II	H	H	H	I	254
III	H	H	H	C_6H_5	204
IV	H	H	I	I	380*
V	H	H	I	C_6H_5	330
VI	H	H	C_6H_5	C_6H_5	280*
VII	H	I	I	I	506*
VIII	H	I	I	C_6H_5	456*
IX	H	I	C_6H_5	C_6H_5	406
X	H	C_6H_5	C_6H_5	C_6H_5	356*
XI	I	I	I	I	632*
XII	I	I	I	C_6H_5	582*
XIII	I	I	C_6H_5	C_6H_5	532*
XIV	I	C_6H_5	C_6H_5	C_6H_5	482
XV	$-C_6H_5$	C_6H_5	C_6H_5	C_6H_5	432

* Parent ion obtained in mass spectrum.

However, with two exceptions, all the naphthalenes identified

by mass spectrometry contain at least two iodine atoms, and no parent ion corresponding to any of the other seven possibilities was observed in any of the mass spectra recorded for the different fractions. One of the exceptions, triphenylnaphthalene(84), was shown (see above) to be a subsequent irradiation product of (56), and if it is assumed, not unreasonably, that the diphenylnaphthalene (108) is also a subsequent irradiation product of (56), then the other six naphthalenes obtained probably still have the two iodine atoms in the 2,3-positions, and the six compounds are probably:- (i) (103), (ii) (101), (iii) (104), (vi) (105), (vii) (107) and (viii) (106); (iv) and (v) are probably (108) and (84), respectively.

The mechanism of the formation of these compounds probably involves an intermediate of type (110), the driving force being the formation of an aromatic compound. (This means that the original premise of

$$RC{\equiv}C{-}I \xrightarrow{h\nu} RC{\equiv}C\cdot + I\cdot$$

is not the only mechanism in this case).

In an attempt to determine whether the mechanism involved ionic addition of hydrogen iodide to the di-iodide(76), (76) was refluxed in benzene, which had been saturated with anhydrous gaseous hydrogen iodide[88]. No substituted naphthalene corresponding to any of the irradiation products was obtained, although starting material could not be recovered from the reaction mixture.

o-Diethynylbenzene(39) was irradiated to investigate whether

or not the above irradiation reaction could be extended to produce naphthalene in this case. Mainly starting material was recovered and no naphthalene was obtained on g.l.c. However, one extra peak was observed in the g.l.c. trace of the reaction mixture which may have been 1-phenylnaphthalene, but this awaits confirmation.

Irradiation of (76) alone, as a thin liquid film, gave, in addition to unchanged starting material, 1,2,3,4-tetra-iodonaphthalene(104), identified by mass spectrometry and hydrogenolysis to naphthalene. No other identifiable product was isolated and mass spectrometry of t.l.c. fractions did not detect the presence of any of the structures (51), (53) or (38), since no molecular ion was observed at 372, 496 or 248 mass units, respectively.

Irradiation of an equimolar mixture of (76) and diphenylacetylene(71), and examination of the product by t.l.c., showed that the diphenylacetylene(71) had taken no part in the reaction, and that the products were the same as had been obtained in the previous irradiation of (76) alone. Once again the desired cyclic poly-yne (52) has not been formed.

In conclusion, it would appear that this type of irradiation reaction, while very useful for the syntheses of simple mono- and di-arylacetylenes, is not very useful for the syntheses of cyclic acetylenes of type (51) and (52), due to the close proximity of the two triple bonds in intermediates of type (76), which tend to react

intra-molecularly under the influence of u.v. irradiation.

EXPERIMENTAL. SECTION 1.

General. Melting points were recorded on a Kofler microscope hot-stage and are uncorrected. Refractive indices were measured on an Abbé refractometer. Routine infrared absorption spectra of liquid films and nujol mulls, were recorded on Perkin-Elmer 137 and 237, and Unicam S.P.200 spectrophotometers, (accuracy ± 10cm.$^{-1}$). Quantitative infrared absorption spectra were determined on a Unicam S.P.100 double-beam spectrophotometer, equipped with an S.P.130 sodium chloride prism-grating double monochromator and operated under vacuum conditions, (accuracy ± 1cm.$^{-1}$). Ultraviolet absorption spectra were recorded on a Perkin-Elmer model 137 u.v. spectrophotometer, and on Unicam S.P.500 and S.P.800 spectrophotometers. Nuclear magnetic resonance spectra were determined on A.E.I. RS2 (60 megacycles) and Perkin-Elmer RS10 (60 megacycles) spectrometers, and mass spectra on A.E.I. MS2 and MS9 spectrometers. Gas-liquid chromatography (g.l.c.) was carried out on a Pye Argon Chromatograph, equipped with a β-ionisation detector, a Perkin-Elmer 451 Fractometer, fitted with a hot-wire detector and a flame-ionisation detector, and a Perkin-Elmer F11, equipped with a flame-ionisation detector. (Retention times were measured at a flow rate of 50ml/min., unless otherwise stated.) Thin layer chromatography (t.l.c.) was carried out with alumina (aluminium oxide G-E.Merck) and silica (Kieselgel G-E.Merck).

Petrol refers to light petroleum fraction, b.p. 40-60°, unless

otherwise stated.

The figures quoted for molecular and other ions in the mass spectra, refer to m/e values unless otherwise stated.

Preparation of 1-iodo-2-phenylacetylene(70).

A solution of phenylacetylene(77) (6.1gm.) in ether (20ml.) was added over 10 min. to a stirred suspension of sodamide in liquid ammonia, prepared in the usual way[89] from sodium (1.5gm.) in liquid ammonia (200ml.) with ferric nitrate (50mg.) as catalyst. Iodine (17gm.) was carefully added, and the reaction mixture stirred overnight. More ether was added, and the reaction worked up by the careful addition of water, and separation of the ether layer. The ether layer was washed thoroughly with water, aqueous sodium thiosulphate solution (to remove iodine), aqueous silver nitrate solution (to remove any unchanged acetylene) and finally with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent and distillation under reduced pressure gave the desired compound (70) (12gm.-88%), as a pale yellow oil, b.p. 115-116°/16mm., n_D^{22} 1.6641. (Manchot[90] gives b.p. 115-117°/16mm. and Vaughn and Nieuwland[78] give n_D^{25} 1.6591.). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.8. The i.r. spectrum (liquid film) was devoid of any absorption in the 3300cm.$^{-1}$ region (ν≡C-H), and had a small peak at~2200cm.$^{-1}$, (νC≡C). The u.v. spectrum (ethanol), had λmax. 250mμ and 259mμ (log ε, 4.22 and 4.16, respectively).

Preparation of o-diethynylbenzene(39).

Potassium (5.1gm.) was dissolved in dry t-butanol (400ml.) and the excess solvent removed under reduced pressure. The residual potassium t-butoxide was then dissolved, with stirring, under reflux, in benzene (500ml.) and a solution of 1-(trans-β-bromovinyl)-2-ethynylbenzene(78) (20.7gm.) in benzene (100ml.) was added dropwise over 30 min. to the opalescent solution, and the mixture heated under reflux for 4 hr. The reaction mixture was then cooled, ether (100ml.) was added, and the mixture shaken with dilute hydrochloric acid. The organic layer was separated, washed with water, aqueous sodium carbonate solution and water, dried (magnesium sulphate) and filtered. The solvent was carefully removed under reduced pressure, and the crude oil fractionally distilled to yield o-diethynylbenzene(39) (9.1gm.-72%) as a pale yellow oil, b.p. 81-82°/14mm., n_D^{20} 1.5908. (Deluchat[91] gives b.p. 80-82°/14mm., $n_D^{17.5}$ 1.5915). The product did not contain halogen (Beilstein test negative), and t.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.55. The i.r. spectrum (liquid film) was identical to that of an authentic sample (provided by Lardy[2]) and showed absorption at ~3300cm.$^{-1}$ (ν≡C-H), and at ~2100cm.$^{-1}$ (νC≡C), but no absorption at ~1650cm.$^{-1}$, (trans-double bond).

Preparation of 1,2-bis(β-iodoethynyl)benzene(76).

(a) Iodine in liquid ammonia method. o-Diethynylbenzene(39) (2.2gm.), as the di-sodium salt in liquid ammonia [from sodium (0.81gm.) in ammonia (75ml.)] was treated with iodine (8.9gm.) as in the preparation of (70). Work up in the usual manner gave a crude dark brown oil (4.16gm.-63%), which would not distil. The i.r. spectrum of the crude product showed a weak band at ~3300cm.$^{-1}$ (ν≡C-H) and a strong band at ~2200cm.$^{-1}$ (νC≡C). T.l.c. (silica - petrol as eluent) was inconclusive, but more than one compound appeared to be present. Attempted purification by chromatography (silica and alumina) was not very successful.

(b) Iodine-morpholine complex method. The complex[79] (79 or 80) of iodine and morpholine was prepared by dissolving iodine (2.8gm.) in aqueous potassium iodide solution and adding morpholine (4.0gm.). The complex was obtained as an orange precipitate which was added to methanol (40ml.). The reaction mixture was stirred and o-diethynylbenzene(39) (600mg.) was added. Stirring was continued at room temperature for 72 hr. and the methanol was then evaporated under reduced pressure, to yield a yellow solid which was extracted with ether, leaving morpholine hydrogen iodide as a pale yellow solid residue, m.p. 212° (decomp.). [Southwick and Kirchner[80] give m.p. 212-213° (decomp.)]. The ethereal extract was washed successively with water, aqueous silver nitrate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent

gave a red oil (1.72gm.-96%) which was not further purified. The i.r. spectrum (liquid film) showed a weak band at ~3300cm.$^{-1}$ ($\nu \equiv C-H$) and a strong band at ~2150cm.$^{-1}$ ($\nu C \equiv C$). The u.v. spectrum (ethanol) had λmax. 234mμ and 242mμ. T.l.c. (silica - petrol as eluent) showed essentially only one spot, R_F 0.3, and the mass spectrum of the fraction corresponding to this spot on preparative t.l.c. showed a molecular ion at 378, ($C_{10}H_4I_2$ requires M.W. 378).

Oxidative coupling of o-diethynylbenzene(39).

Anhydrous cupric acetate (750mg.) was dissolved in pyridine (10ml.) and methanol (10ml.), and o-diethynylbenzene(39) (130mg.) added all at once. The reaction mixture was heated under reflux for 4 hr., cooled, and poured into dilute sulphuric acid and ice. The aqueous mixture was extracted three times with ether, and the combined ethereal extracts washed successively with dilute sulphuric acid, water, saturated aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a brown solid (120mg.), which on t.l.c. (silica - 20% ethyl acetate-petrol as eluent) showed one distinct spot (yellow before staining), R_F 0.7, and several less distinct ones. A portion of this crude material (20mg.) was purified by preparative t.l.c. (silica, 1mm. thick - eluted with 20% ethyl acetate-petrol). The fastest moving band (yellow coloured in visible light) on elution gave 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne

(38) (9mg.), m.p. ~80° (decomp.), identical (i.r. and u.v.) with the properties already given[1,2]. No satisfactory analysis had previously been obtained for this compound[1,2], and proof of structure is given by the X-ray measurements[2,63]. The mass spectrum not only showed the expected molecular ion and (molecular weight + one) ion, (due to C_{13}), at 248 and 249, respectively, ($C_{20}H_8$ requires M.W. 248), but also significant parent ions at 250 and 252, plus (parent + one) ions at 251 and 253, respectively, corresponding to two and four more hydrogens, respectively, than required. Thus it would appear that some ene-triyne (61) and diene-diyne (62 or 63) have also been formed in this coupling reaction. It should be pointed out that this sample was not recrystallised from benzene, whereas the X-ray sample was, which could account for these other compounds (61 and 62 or 63) not being reported before. Also the reaction has been carried out at a different concentration than previously reported. Repeated t.l.c. of this yellow crystalline mixture, still showed one spot, even on silica which had been impregnated with silver nitrate. Attempted separation by g.l.c. was unsuccessful.

Cutting the preparitive plate into several bands and elution of each, gave several other small fractions, all of which had rather uninteresting u.v. spectra, and no compound corresponding to the hoped for "triangular" structure (51) was obtained, since mass spectra of several of the fractions, while giving no indication of the structures of these compounds, definitely precluded a molecular

weight of 372, ($C_{30}H_{12}$ requires M.W. 372).

Irradiation of 1-iodo-2-phenylacetylene(70) in benzene.

A solution of (70) in benzene was securely stoppered in a quartz tube after flushing out with nitrogen, and irradiated in a stream of cold air for 24 hr. The temperature, at the end of several runs, was found to be only a few degrees above room temperature. The lamp used for the irradiation was a low-pressure mercury lamp, emitting mainly radiation of wavelength 2537Å. After the irradiation, the benzene solution was washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate), filtered and evaporated.

In this way, 1-iodo-2-phenylacetylene(70) was irradiated in benzene at four different concentrations.

(i) 1.01gm. in 50ml. (1 mole in 125 moles). The crude solid obtained on removal of the benzene, was chromatographed on alumina (Brockmann Grade I; 30gm.). Elution with petrol gave a colourless solid, (630mg.-79%) needles, m.p.61°, from aqueous ethanol. The crystalline compound was shown to be diphenylacetylene(71) by t.l.c., u.v. and mixed m.p. comparison with an authentic sample. The crude solid had previously been shown to contain no trace of diphenyldiacetylene(75) by t.l.c. and u.v. [(71) is transparent above 300mμ, whereas (75) has a prominent band at 327mμ (log ε, 4.50), which would have been detectable, even at concentrations down to about 1%].

However, t.l.c. (silica - petrol as eluent) did show three additional spots, R_F 0.2, 0.3 and 0.4. [The R_F of (71) is 0.65, that of (75) being 0.6]. These additional compounds were only present in trace amounts, and only showed as faint blue fluorescent spots when the chromatoplate was viewed under u.v. light.

(ii) 100mg. in 50ml. (1 mole in 1280 moles). Again the only compounds obtained in this irradiation were (71), t.l.c. and u.v., and the compounds corresponding to the same three spots as before on t.l.c., R_F 0.2, 0.3 and 0.4.

(iii) 10mg. in 50ml. (1 mole in 12800 moles). In this case, only the spots on t.l.c. of R_F 0.3 and 0.4 could be detected in addition to that corresponding to (71), and these were very faint.

(iv) 1gm. in 2ml. (1 mole in 5 moles). T.l.c. in this case, did reveal a faint red spot, R_F 0.6, below the yellow spot, R_F 0.65, which is characteritic of (71). The spots of R_F 0.2, 0.3 and 0.4 were also present. (75) also gives rise to a red spot on t.l.c., R_F 0.6, and the diphenyldiacetylene(75) was estimated to be present in about 3%, based on the relative intensities of the 296mμ band of (71) (log ε, 4.48) and the 327mμ band of (75) (log ε, 4.50) in the u.v. spectrum of the crude product.

Irradiation of diphenylacetylene(71) in benzene.

A solution of diphenylacetylene(71) (220mg.) in benzene (25ml.) was irradiated under nitrogen in a quartz tube for 24 hr. as before.

After 24 hr., the colourless solution had turned yellow. T.l.c. (silica - petrol as eluent) showed, when viewed under u.v. light, in addition to unchanged starting material, R_F 0.65, three blue fluorescent spots, R_F 0.2, 0.3 and 0.4.

Irradiation of diphenylacetylene(71) in hexane.

A solution of (71) (200mg.) in hexane (25ml.) was irradiated for 24 hr. as before. T.l.c. (silica - petrol as eluent), showed unchanged (71), R_F 0.65, and three blue fluorescent spots, R_F 0.2, 0.3 and 0.4.

Irradiation of 1-iodo-2-phenylacetylene(70) in carbon tetrachloride.

A solution of (70) (515mg.) in carbon tetrachloride (50ml.) was irradiated as before for 24 hr., washed with aqueous sodium thiosulphate solution and water, dried (sodium sulphate) and filtered. Evaporation of the solvent gave an oil, which on t.l.c. (silica - petrol as eluent) showed only a large yellow fluorescent spot when viewed under u.v. light, tailing just above the origin.

Irradiation of 1-iodo-2-phenylacetylene(70) in cyclohexane.

A solution of (70) (550mg.) in cyclohexane (50ml.) was irradiated as before for 24 hr., washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. T.l.c. (silica - petrol as eluent) showed two faint spots, R_F 0.5

and 0.25, and a large spot on the origin. No spot corresponding to diphenyldiacetylene(75) was detected. Evaporation of the solvent gave an oil, whose i.r. spectrum (liquid film) showed absorption at~3300cm.$^{-1}$, ($\nu\equiv$C-H).

Irradiation of phenylacetylene(77) in cyclohexane.

A solution of (77)(500mg.) in cyclohexane (25ml.) was irradiated as before for 24 hr. T.l.c. (silica - petrol as eluent) showed three faint spots, R_F 0.5, 0.25, and 0.15, and a large spot which had not moved from the origin. Evaporation of the solvent gave an oil, which still contained a large percentage of unchanged starting material; i.r. (liquid film), large peak at~3300cm.$^{-1}$ ($\nu\equiv$C-H). The starting material could not be detected by t.l.c., due to its volatility.

Irradiation of 1-iodo-2-phenylacetylene(70) as a thin film.

A thin liquid film of (70) (1.08gm.) on the sides of a quartz tube, sealed under nitrogen as in the previous experiments, was irradiated for 24 hr.. At the end of the irradiation, the film had set as a glass. This was dissolved in hot benzene, cooled, washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a crude oily-solid, which on chromatography over silica (50gm.) and elution with petrol, gave unchanged starting material (70)

(415mg. - 38%), identified by i.r., u.v. and t.l.c. (silica - petrol as eluent, R_F 0.8). Elution with 5% ether-petrol gave diphenyldiacetylene(75), (130mg. - 27%), needles m.p. 87-88° from aqueous ethanol, shown to be identical with an authentic sample by i.r., u.v., t.l.c. and mixed m.p. behaviour. The crude semi-solid, prior to chromatography, was shown by t.l.c. (silica - petrol as eluent) to contain, in addition to (70), R_F 0.8, and (75), R_F 0.6, several faint spots, R_F 0.7, 0.45, 0.4, 0.3, 0.15, 0.1.

Irradiation of diphenyldiacetylene(75) in benzene.

A solution of (75) (220mg.) in benzene (25ml.) was irradiated as before for 24 hr. T.l.c. (silica - petrol as eluent) showed only unchanged starting material (75), R_F 0.6.

Irradiation of di-iodoacetylene(99) in benzene.

A solution of (99) (1.29gm.) in benzene (50ml.) was irradiated as before for 24 hr. The benzene solution was washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a dark viscous oil (770mg.). T.l.c. (silica - petrol as eluent) showed that diphenylacetylene(71) was present, R_F 0.65, but although unchanged starting material (99) could be detected in the oil by its characteristic unpleasant odour, t.l.c. was insensitive to it. Other spots were present in the chromatogram at R_F 0.9, 0.85 and 0.1, but no spot

at R_F 0.8, corresponding to (70), could be detected. The u.v. spectrum of the crude oil confirmed the presence of (71) by the characteristic peaks at 264mμ, 272mμ, 279mμ, 288mμ and 296mμ. Attempted isolation of (71) by chromatography on silica (30gm.) was unsuccessful, evaporation of successive fractions (petrol - as eluent) yielding only dark foul-smelling oils, shown by t.l.c. to contain several other spots in addition to that corresponding to (71).

Irradiation of 1,2-bis(β-iodoethynyl)benzene(76) in benzene.

A solution of (76) (270mg.) in benzene (27ml.) was irradiated for 24 hr. as before. The benzene solution was washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a yellow oil (165mg.), whose i.r. spectrum showed strong peaks at ~750cm.$^{-1}$ and ~680cm.$^{-1}$ (mixture of mono- and 1,2-di-substituted aromatic rings). T.l.c. (silica - petrol as eluent) showed five spots (the first four pale yellow in visible light), R_F 0.6, 0.5, 0.45, 0.3 and 0.2, with a u.v. fluorescent spot at 0.15. Attempted separation of the compounds by chromatography (silica and alumina - petrol as eluent), resulted in mixtures of compounds. Successful separation was achieved on a small scale by preparative t.l.c. (1mm. thick - 20mg. loading - eluted three times with petrol).

(i) The fraction corresponding to the spot of R_F 0.6 was obtained

(~2mg.) as pale yellow needles, m.p. 89-91°. The i.r. spectrum (nujol mull) showed strong absorption at ~745cm.$^{-1}$ and very weak absorption at ~725cm.$^{-1}$. The u.v. spectrum (cyclohexane) had λmax 243mμ, 297mμ, 310mμ, 335mμ and 352mμ, (log ε 4.07, 3.89, 3.81, 4.0 and 3.82, respectively), (Fig.2). The mass spectrum showed a molecular ion at 506, ($C_{10}H_5I_3$ requires M.W. 506), plus large ions at 379, 252 and 125, with metastable ions at 283.8, 167.6 and 62.0, corresponding to losses of 127, 127 and 127, respectively. That this compound was one of the tri-iodonaphthalenes (101) or (102), was confirmed by hydrogenolysis in ethyl acetate, using 5% palladium on charcoal as catalyst. Naphthalene was obtained, identified on g.l.c. [5% Apiezon "L" grease on Celite (80-100 mesh) at 100° - retention time, 7 min.] by comparison with an authentic sample.

The ratio of the peak at 380 to that at 379 in the mass spectrum, was larger than expected for the normal C^{13} contribution, and this, together with the small ion at 381, suggests that a compound [probably (103)] of molecular weight 380 is present, [(103), $C_{10}H_6I_2$ requires M.W. 380].

(ii) The fraction corresponding to the spot of R_F 0.5 was obtained as an oil (~1mg.), and showed i.r. absorption (liquid film) at ~750cm.$^{-1}$, a shoulder at ~730cm.$^{-1}$ and a band at ~700cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 244mμ, 289mμ, 301mμ and 336mμ. That this fraction contained two compounds, was shown by the mass

spectrum, which showed a small parent ion at 632,[due to (104), $C_{10}H_4I_4$ requires M.W. 632] and a large parent ion at 456, [due to (105), $C_{16}H_{10}I_2$ requires M.W. 456], with a large ion at 329 and a metastable ion at 237.3, corresponding to the loss of 127 from 456 to 329. This fraction was hydrogenolysed in ethyl acetate as before. The u.v. spectrum (ethanol) of the crude product was similar to that of 1-phenylnaphthalene.

(iii) The fraction corresponding to the spot of R_F 0.45 was obtained as an oil (~1mg.). The i.r. spectrum (liquid film) showed a strong absorption band at ~730cm.$^{-1}$, a weak band at ~735cm.$^{-1}$ and a medium band at ~710cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 243mμ, 285mμ, 305mμ and 335mμ. The mass spectrum showed a molecular ion at 582, [(106), $C_{16}H_9I_3$ requires M.W. 582], with large ions at 455 and 328, and metastable ions at 355.7 and 236.4, corresponding to losses of 127 and 127, respectively. This fraction was hydrogenolysed in ethyl acetate as before. The u.v. spectrum (ethanol) of the crude product was similar to that of 1-phenylnaphthalene.

(iv) The fraction corresponding to the spot of R_F 0.3 was obtained as an oil (~1mg.). The i.r. spectrum (liquid film) showed absorption at ~760cm.$^{-1}$ and ~700cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 247mμ, 273mμ, 290mμ and 308mμ. The mass spectrum showed a molecular ion at 532,[(107), $C_{22}H_{14}I_2$ requires M.W. 532], with large ions at 405 and 278, and metastable ions at 308.3 and

190.8, corresponding to losses of 127 and127, respectively. The peak at 280 was also significant, and indicates that (108) may also be present, ($C_{22}H_{16}$ requires M.W. 280).

(v) The last fraction, corresponding to the faint spot of R_F 0.2 and the fluorescent spot of R_F 0.15, which could not be separated, was obtained as a yellow oil (11mg.). It was shown to be a mixture of mainly (56) and a trace of (84). The i.r. spectrum (liquid film) showed absorption at ~2200cm.$^{-1}$ ($\nu C{\equiv}C$), ~770cm.$^{-1}$ and ~7[illegible]cm.$^{-1}$, and was virtually identical to that obtained from the more conventional preparation of the hydrocarbon (56), (Section II). The u.v. spectrum (ethanol) was again almost identical to that of (56); λmax 259mμ, 273mμ and 312mμ, with an extra small hump at 294mμ, presumably a contribution of (84). The mass spectrum showed a large molecular ion at 278, [(56), $C_{22}H_{14}$ requires M.W. 278], together with a much smaller molecular ion at 356, probably due to (84), ($C_{28}H_{20}$ requires M.W. 356).

Irradiation of 1,2-bis(β-phenylethynyl)benzene(56) in benzene.

A solution of (56) (80mg.) in benzene (3ml.) was irradiated as before for 24 hr. T.l.c. of the solution (silica - petrol as eluent) showed mainly unchanged (56), R_F 0.15, with a faint yellow spot just above it. Preparative t.l.c. (1mm. thick plate) and cutting the band just above the band of (56), gave, on elution with ethyl acetate, sufficent material for a mass spectrometric

determination. This showed a large parent ion at 278, [due to (56), $C_{22}H_{14}$ requires M.W. 278] and a much smaller parent ion at 356, [due to (84), $C_{28}H_{20}$ requires M.W. 356].

Irradiation of 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne(38) in benzene.

A solution of (38) (10mg.) in benzene (1ml.) was irradiated as before for 24 hr. T.l.c. of this solution (silica - petrol as eluent) showed mainly unchanged starting material (38), R_F 0.15, with only a new faint fluorescent spot just above the origin.

Irradiation of o-diethynylbenzene(39) in benzene.

A solution of (39) (510mg.) in benzene (25ml.) was irradiated as before for 24 hr. G.l.c. of this solution [5% Apiezon "L" grease on Celite (80-100 mesh) at 100°] did not show a peak corresponding to naphthalene, although a peak (retention time 19 min.) was observed in addition to the main peak (retention time 4 min.), due to unchanged (39). T.l.c. (silica - petrol as eluent) showed, in addition to the spot corresponding to (39), R_F 0.55, a spot of R_F 0.35.

Irradiation of 1,2-bis(β-iodoethynyl)benzene(76) as a thin liquid film.

A thin film of (76) (100mg.) on the sides of a quartz tube, was irradiated under nitrogen as before for 24 hr. The liquid film

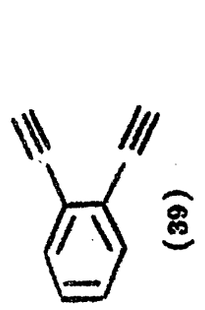
was then dissolved in benzene, washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a dark oil (75mg.). T.l.c. (silica - petrol as eluent) showed three main spots, R_F 0.5, 0.3 and 0.05. The i.r. and u.v. spectra of the crude oil were virtually identical to those of the starting di-iodide (76). Preparative t.l.c. was carried out on a portion of the crude oil (20mg.), and three fractions were eluted. The fraction corresponding to the spot just above the origin, R_F 0.05, was obtained as a brown amorphous solid (~1mg.). Mass spectrometric analysis revealed no obvious parent ion. The fraction corresponding to the spot of R_F 0.3, was shown to be unchanged starting material (76) (14mg.), by i.r. and u.v. comparison, and by its mass spectrum; molecular ion at 378, ($C_{10}H_4I_2$ requires M.W. 378). The fraction corresponding to the spot of R_F 0.5 (yellow in visible light) was obtained as pale yellow crystals, m.p. 97-98°, (~2mg.). The i.r. spectrum (melted film) showed absorption at ~750cm.$^{-1}$ (1,2-di-substituted aromatic ring), and the mass spectrum, showed a molecular ion at 632, ($C_{10}H_4I_4$ requires M.W. 632), plus large ions at 505, 378, 251 and 124, with metastable ions at 403.5, 282.9, 156.7 and 31.3, corresponding to losses of 127, 127, 127 and 127, respectively. Hydrogenolysis in ethyl acetate, using 5% palladium on charcoal as catalyst, gave naphthalene, identified on g.l.c. by comparison with an authentic sample, as before. This compound is presumably 1,2,3,4-tetra-iodonaphthalene(104).

Irradiation of 1,2-bis(β-iodoethynyl)benzene(76) in diphenylacetylene(71).

An equimolar solution of (76) (52mg.) and (71) (24mg.) in a small volume of ether was placed in a quartz tube, and the ether allowed to evaporate, distributing a thin film around the sides of the tube. The tube was flushed out with nitrogen, and irradiated as before for 24 hr. The film was then dissolved in benzene, and the benzene solution washed with aqueous sodium thiosulphate solution and water, dried (magnesium sulphate) and filtered. T.l.c. of the solution (silica - petrol as eluent) showed that the reaction mixture was identical to that of the previous experiment, with the exception of unreacted (71), R_F 0.35.

Reaction of 1,2-bis(β-iodoethynyl)benzene(76) with gaseous hydrogen iodide.

Dry benzene (25ml.) was saturated with anhydrous gaseous hydrogen iodide[38], and (76) (214mg.) was added. The reaction mixture was heated under reflux for 3 hr., and the solution, which had turned purple, was examined by t.l.c. (silica - petrol as eluent). No spots corresponding to those given when (76) was irradiated in benzene were obtained, and the starting material (76) was also absent.



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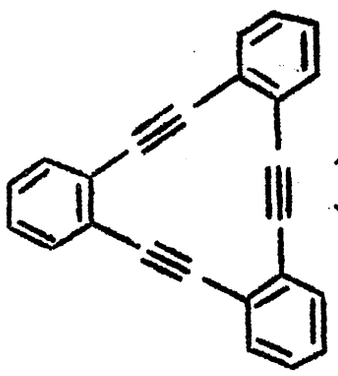

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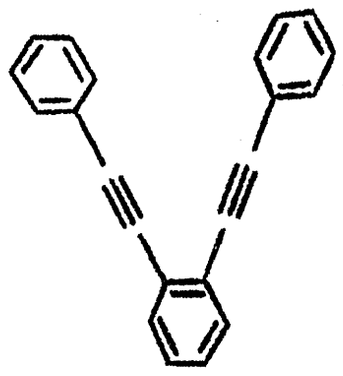

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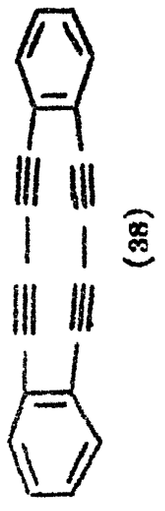

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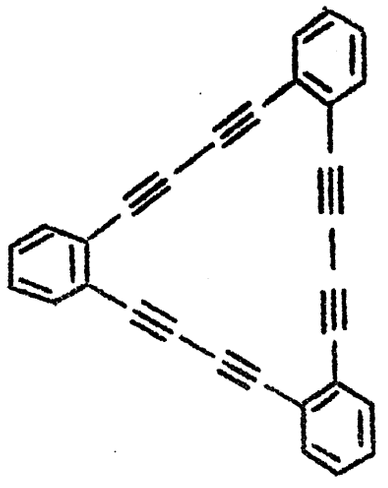

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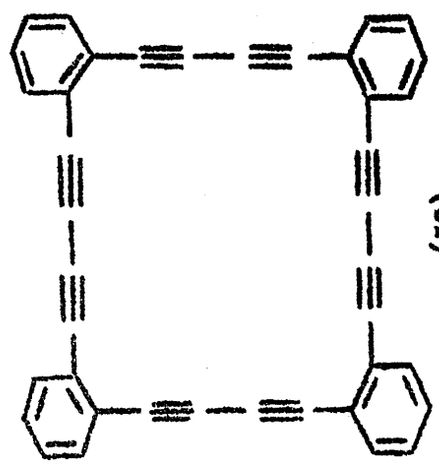

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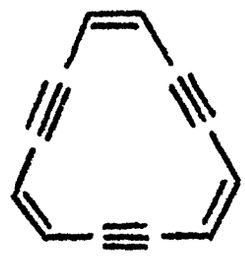

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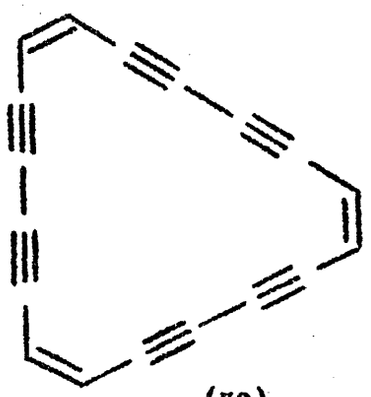

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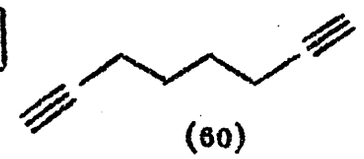

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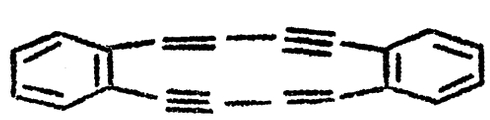

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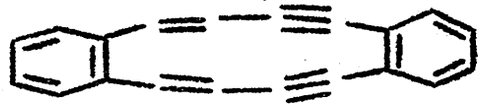

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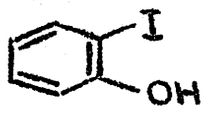

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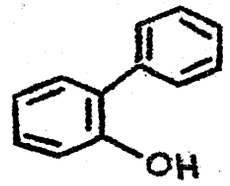

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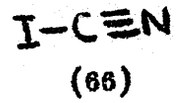

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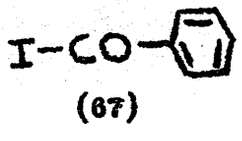

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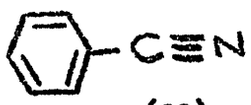

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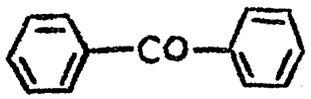

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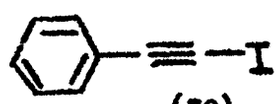

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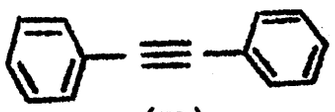

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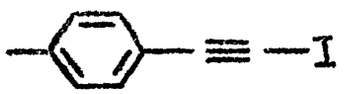

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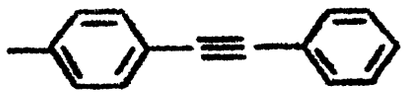

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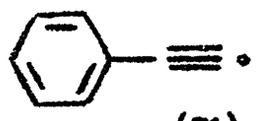

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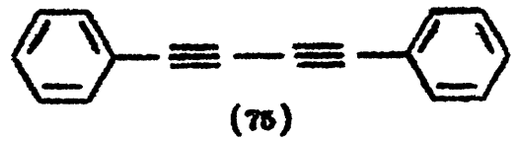

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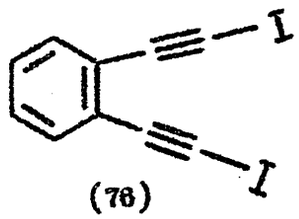

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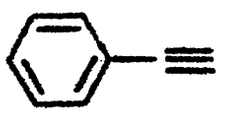

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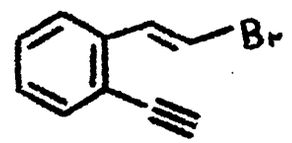

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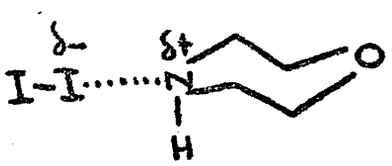

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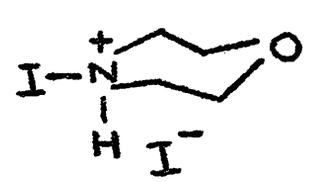

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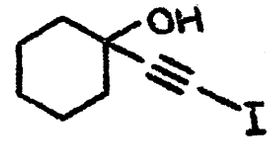

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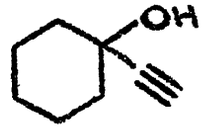

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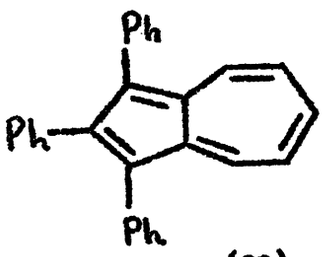

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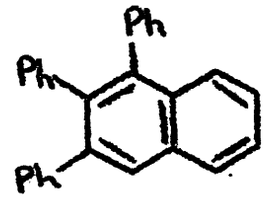

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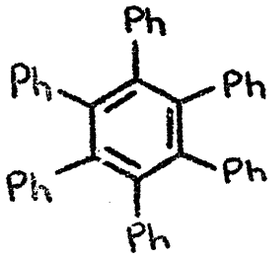

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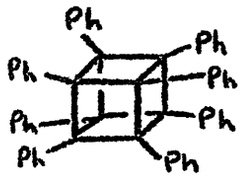

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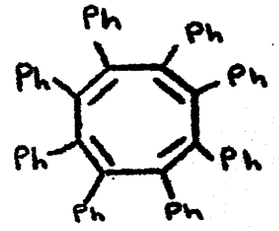

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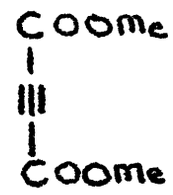

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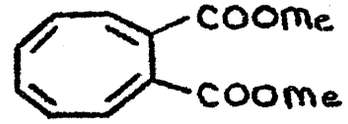

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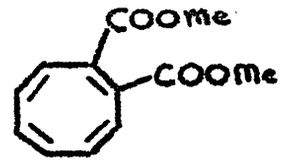

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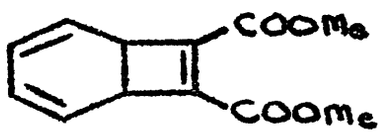

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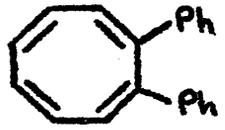

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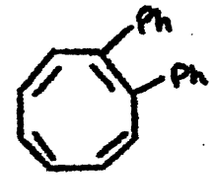

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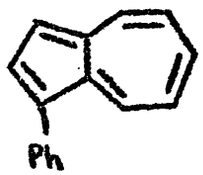

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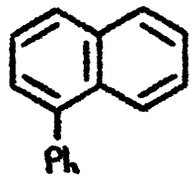

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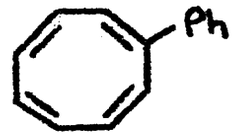

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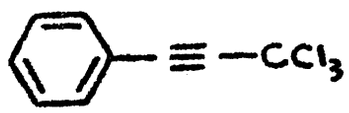

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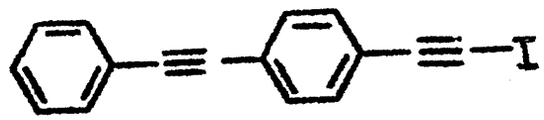

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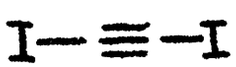

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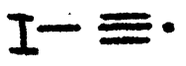

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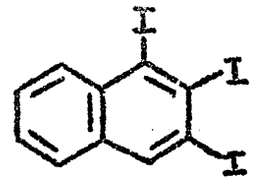

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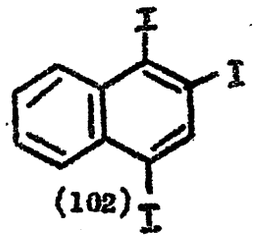

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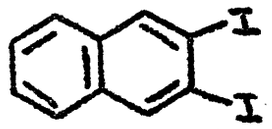

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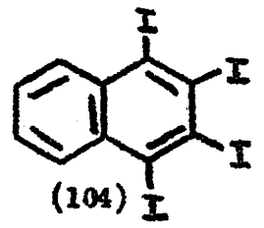

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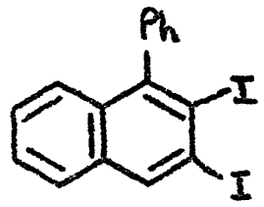

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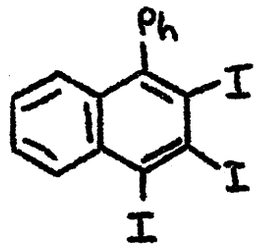

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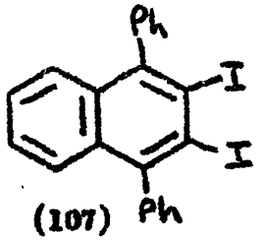

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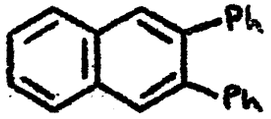

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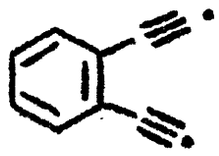

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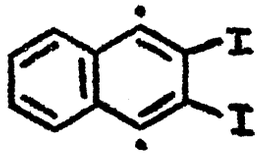

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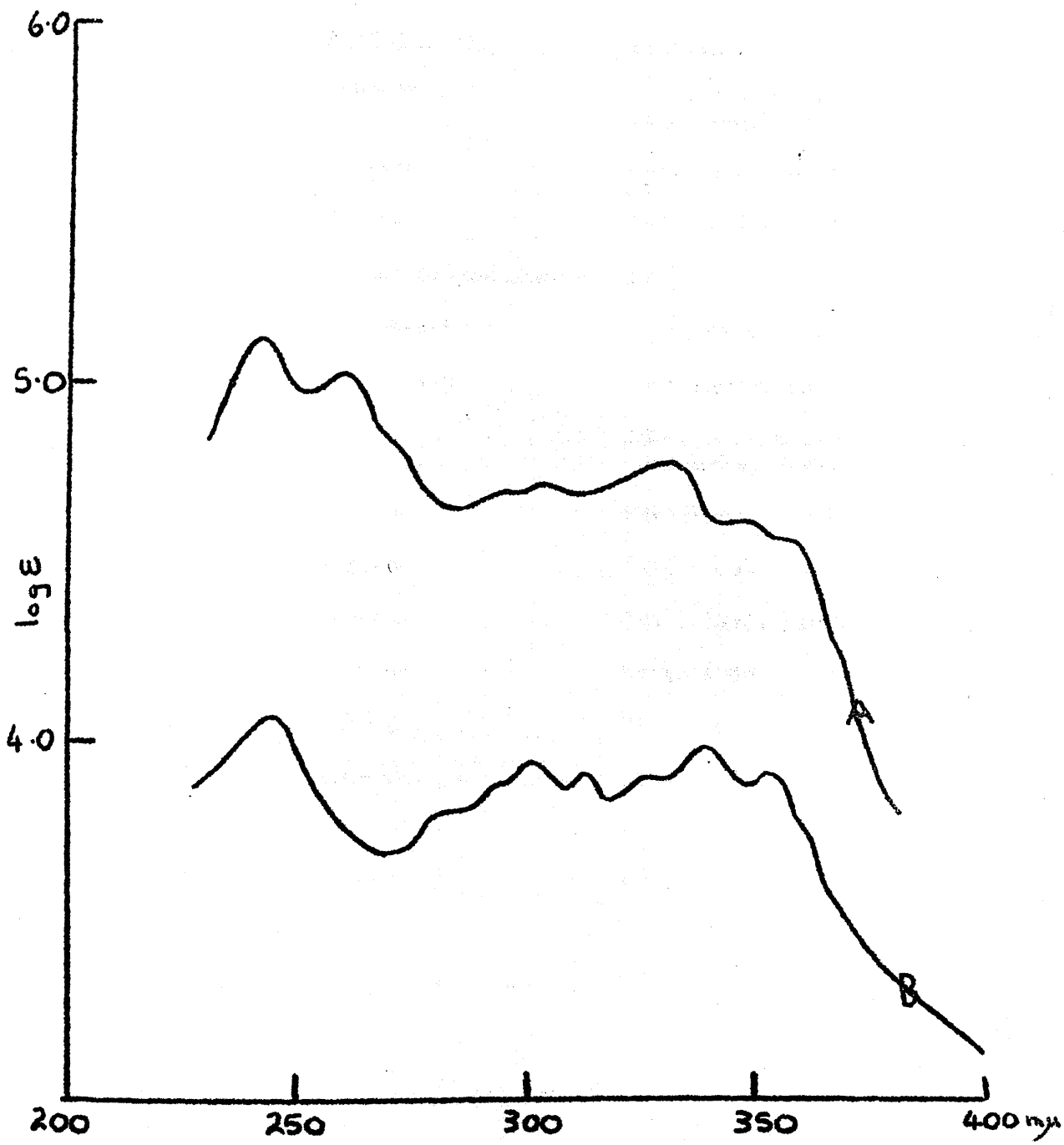


Fig.2.

U.v. spectra:-
A, (53) in ether[1],
B, (101) in cyclohexane.

TABLE 2 - IRRADIATION REACTIONS.

Compound.	Solvent.	Products.
(70)	Benzene	(71), trace (75), plus three other compounds*.
(71)	Benzene	Three compounds*.
(71)	Hexane	Three compounds*.
(70)	Carbon tetrachloride	(97)†.
(70)	Cyclohexane	(77), plus three other compounds[a].
(77)	Cyclohexane	Four compounds[a].
(70)	———	(75), plus several other compounds, probably of type (98)†.
(75)	Benzene	Unchanged.
(99)	Benzene	(71), plus three other compounds.
(73)	Benzene	(56), (84), (101), (104-108).
(56)	Benzene	Trace (84).
(38)	Benzene	Trace unknown.
(39)	Benzene	Trace (95)†.
(76)	———	(104).
(76)/(71)	———	(104).

*Shown by t.l.c. to be the same.

†Tentative.

[a]Shown by t.l.c. to be almost the same.

SECTION II

ATTEMPTED SYNTHESIS OF 1,2:5,6:9,10-TRIBENZO-CYCLODECA-1,5,9,-TRIENE-3,7,11-TRIYNE.

The attempted synthesis of the previously described (Section I) macrocyclic acetylenic hydrocarbon (52), and the synthesis of the related hydrocarbon (56), are described in this section.

The first route to (52), and also to (56), was based on the hydrocarbons (115) and (116). These hydrocarbons,(115) and (116), have been described by Griffin, Martin and Douglas[92], who prepared them,in good yield, via the Wittig reaction[93] of the bis-phosphonium salt (112) with benzaldehyde(113) and o-tolualdehyde(114), respectively.

Bromination of (115) and (116), to the tetrabromides (117) and (118), respectively, followed by successful dehydrobromination, would lead to the hydrocarbons (56) and (119),respectively. Treatment of (119) with N-bromosuccinimide[94] should give the dibromide (120), which, on reaction with sodamide in liquid ammonia, might be expected to yield the hydrocarbon (121). This type of reaction is well known[95-101], e.g., base treatment of the bromide (122) gives the hydrocarbon (123)[95], and phenanthrene(125) can be obtained, in a similar way, from the dibromide (124)[99]. The hydrocarbon (121) has the desired carbon skeleton, and on bromination, followed by dehydrobromination, might afford the desired structure (52).

Alternatively, the dibromide (120) could be converted into the di-aldehyde (126), either by direct oxidation[102-105], or by manganese dioxide oxidation[106] of the corresponding alcohol, formed

from the dibromide (120), via treatment with silver nitrate in aqueous acetone[107]. A simple benzoin condensation[108] on the dialdehyde (126), followed by oxidation, should give the corresponding benzil[109]. Treatment of the bis-hydrazone of this benzil with yellow mercuric oxide[110,111], should afford (52).

Although the hydrocarbon (56) was successfully prepared, structure (52) was not realised by the method outlined above; the relevant details are described below.

The hydrocarbon (115) was prepared according to the reported method[92]. T.l.c. examination of the hydrocarbon mixture obtained, revealed the presence of at least four compounds. Separation of these four compounds for characterisation was achieved by careful chromatography on silica, impregnated with silver nitrate (25%).

The first compound eluted from the column (3%), was shown to be 2-methyl-cis-stilbene(127), by its i.r., u.v., n.m.r. and mass spectra.

The second fraction was likewise identified as the trans-isomer, 2-methyl-trans-stilbene(128) (10%). It is interesting to note that in the n.m.r. spectrum of this compound, the two olefinic protons cannot be distinguished from the aromatic protons. This was not expected, since the olefinic protons in trans-stilbene(129) itself, (singlet at 2.90τ), can be distinguished from the aromatic protons, (multiplet at ~2.6τ)[112]. (See Table 3).

The cis-isomer (127) could be converted into the trans-isomer

(128), by treatment with iodine[113,114]. Bromination of either isomer to the dibromide (131), followed by dehydrobromination, gave 2-methyldiphenylacetylene(132), in good yield. The u.v. spectrum of this compound is discussed in Section III.

These two hydrocarbons (127 and 128) were not reported by the previous workers[92], but their formation can be readily explained, since it is well known[115,116] that hydrolysis of a Wittig salt to give triphenylphosphine oxide and the parent hydrocarbon, is a rapid alternative reaction to condensation with a carbonyl function.

The last two fractions eluted on chromatography were not obtained as pure compounds. However, spectroscopic techniques revealed that they were, in fact, the cis-cis- and cis-trans-isomers of the required hydrocarbon (115). Although the n.m.r. spectra are fully in accord with the proposed structures (Table 3), Griffin, Martin and Douglas[92] reported that the hydrocarbon (115) which they isolated from the condensation was the trans-trans-isomer. Under the conditions employed for this reaction, the Wittig reaction normally produces mixtures of the cis- and trans-isomers[113,114], and it now appears that in this case, the trans-trans-isomer is least favoured.

Nevertheless, the isomeric mixture of (115) was brominated in ether to give the tetrabromide (117), which did not melt sharply, since it was presumably a mixture of the d, l, and meso stereoisomers. Dehydrobromination of this mixture with potassium hydroxide in

triethylene glycol gave the desired hydrocarbon (55). The u.v. spectrum of this compound (Fig.3) was rather remarkable in that it did not resemble that of the parent hydrocarbon (71), whereas, in a similar series, the hydrocarbon (55) has a u.v. spectrum which is very similar to that of the related diphenyldiacetylene (75), (Fig.4). The explanation of this phenomenon possibly lies in the fact that the two terminal benzene rings are so close to one another, that they have to lie parallel to one another, thus modifying the conjugation with the central ring.

In order to confirm the carbon skeleton of (56), this hydrocarbon was hydrogenated, and compared with an authentic sample of the expected hydrocarbon (133), prepared by hydrogenation of (115). Both these hydrogenations proceeded smoothly, and only the hydrocarbon (133) was isolated in each case.

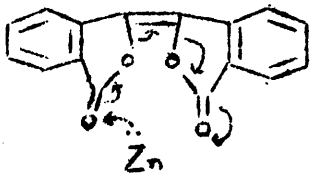
Returning to the synthesis of (52), via the hydrocarbon (116), the bis-phosphonium salt (112) was condensed with o-tolualdehyde (114) in the manner described by Griffin, Martin and Douglas[92]. However, despite several attempts, (116) was not isolated from this reaction, the main products, later identified by comparison with authentic samples, (see below), being the cis- and trans- isomers of 2,2'-dimethylstilbene(134 and 135, respectively). This route was therefore abandoned, and attention turned to an alternative synthesis, also based on the Wittig reaction.

The condensation of o-phthaldialdehyde(136) with either of the

Wittig salts (137) or (112), leads to the hydrocarbons (138)[92] and (139)[117], respectively, and it was felt that condensation of the di-aldehyde (140) with the bis-phosphonium salt (112), might lead to the hydrocarbon (141), which has the desired carbon skeleton. Alternatively, condensation of o-phthaldialdehyde(136) with the Wittig salt (142), could lead to the same hydrocarbon (141).

A possible intermediate in the in the synthesis of the di-aldehyde (140), is 2,2'-tolanedicarboxylic acid, (diphenylacetylene-2,2'-dicarboxylic acid) (143). This acid (143), via the bis-methyl ester (144), reduction with lithium aluminium hydride to the diol (145), and oxidation with manganese dioxide[106], should afford the required di-aldehyde (140).

The readily available diphthalyl(146), obtainable in one step from phthalide(147) and phthalic anhydride(148)[118], was chosen as the starting material for preparation of the di-acid (143), since it was possible that zinc reduction of (146), would lead directly to the zinc salt of the acid as shown.



However, although reduction of diphthalyl(146) with zinc in acetamide appeared to give some acidic material, the desired compound (143) could not be extracted from the reaction mixture. Nor could

the ester (144) be isolated following direct esterification of the crude reaction mixture. As a synthetic route to the dialdehyde (140), this reaction scheme was not very promising, and this approach was abandoned.

Since this work was completed, Letsinger, Oftedahl and Nazy[119] have prepared 2,2'-tolanedicarboxylic acid(143), by direct carboxylation of 2,2'-dilithiodiphenylacetylene(149), an unstable intermediate obtained by treating 2,2'-dibromodiphenylacetylene(150) with butyllithium. This acid (143) was found to be very reactive, lactonising readily in an ethanolic solution at room temperature to give (151), which could be converted into the alternative lactone (152).

Ruggli and Meyer[120] also claim to have isolated only a lactone when they attempted to prepare 2,2'-tolanedicarboxylic acid(143) by bromination and dehydrobromination of 2,2'-stilbenedicarboxylic acid.

Attention was therefore concentrated on the alternative scheme based on the bis-phosphonium salt (142). o-Xylene(153), the starting material for the synthesis of this Wittig salt (142), was brominated in the usual way[121] to give (154). Attempted preparation of 2,2'-dimethylstilbene(134 or 135) directly from (154), by reaction with sodamide in liquid ammonia, which readily converts benzyl chloride(155) into trans-stilbene(129)[100], was unsuccessful. The desired stilbene (134 or 135) was prepared by condensing

o-tolualdehyde(114) with the phosphonium salt (153), from the bromide (154). A mixture of cis- and trans-isomers was obtained [c.f. the preparation of (115)], the n.m.r. spectra again being interesting. (Table 3). Bromination to the dibromide (157), followed by dehydrobromination, led to 2,2'-dimethyldiphenylacetylene(158). In large scale preparations of this hydrocarbon (158), 2,2'-dimethyl-trans-stilbene(135) was also occasionally isolated, and this reaction was investigated further. Several dibromides were treated with different reagents under varying conditions. The results are summarised in Table 4, and the relevant conclusions are listed below.

(a) The stilbenes appear to be formed by a thermal cis-elimination of bromine.

(b) The d,l-dibromides appear to eliminate bromine more readily than the meso-dibromides.

(c) The elimination also takes place in ether solvents, and therefore does not require a protonated solvent.

(d) This side reaction can be considerably reduced by ensuring that the potassium hydroxide is completely in solution before adding the dibromide.

Returning to the synthesis of the Wittig salt (142), treatment of the hydrocarbon (158) with N-bromosuccinimide[94] led to a mixture of the mono- and di-bromides (159) and (160), respectively, which were quite easily separated by column chromatography. Reaction of the dibromide (160) with triphenylphosphine in dimethylformamide,

led to the desired bis-phosphonium salt (142).

The Wittig reaction was carried out as before by treating a mixture of the bis-phosphonium salt (142) and o-phthaldialdehyde (136) in ethanol, with an ethanolic solution of lithium ethoxide. The crude solid obtained on evaporation of the solvent, was extracted thoroughly with hot petrol, and gave, on evaporation of the petrol, a high-melting, yellow crystalline solid, which was shown by t.l.c. to be a mixture of compounds. This mixture could not be separated, either by column chromatography or by preparative t.l.c. Purification by sublimation or recrystallisation, was also unsuccessful. However, a carbon-hydrogen analysis indicated that the mixture contained mainly hydrocarbons, and the i.r. spectrum showed strong absorption at ~ 970cm.$^{-1}$, which is characteristic of a trans-double bond. The desired hydrocarbon (141), appears to be present, since hydrogenation of a portion of the crude product produced the expected hydrocarbon (162), identified by g.l.c. comparison with an authentic sample [prepared roughly according to the method of Cope and Fenton[122]].

Also, using the technique of mass spectrometry combined with t.l.c., a molecular ion at 304 was observed for one fraction, [(141), $C_{24}H_{16}$ requires M.W. 304].

Although the hydrocarbon (141) could not be isolated from the reaction mixture, bromination followed by dehydrobromination experiments were carried out [which were expected to convert (141)

to (52)]. However, despite several attempts, no compound was isolated which showed any exceptional bands in the u.v. spectrum, and therefore the hydrocarbon (52) does not appear to have been formed.

The nature of the other two compounds from the Wittig condensation, detected by t.l.c. (and by g.l.c.) is not known, but while it is attractive to postulate that the three compounds are the cis-cis-, the cis-trans- and the trans-trans-isomers of (141), this does not appear to be the case, since they were not apparently isomerised on treatment with iodine as before.

The last route to the hydrocarbon (52) was based on the report by Castro and Stephens[123], that heating a mixture of cuprous phenylacetylide(165) and iodobenzene(166) under reflux in pyridine, in an atmosphere of nitrogen, led to diphenylacetylene(71) in good yield. This reaction was repeated, and (71) was isolated in good yield, although some oxidatively coupled product, (75) could also be detected in the reaction mixture. (See Section IV).

Extension of this type of reaction could lead to the hydrocarbon (52), either from similar treatment of a mixture of 2,2'-di-iododiphenylacetylene(167) and the bis-cuprous salt of o-diethynylbenzene(168), or directly from cuprous o-iodophenylacetylide (169).

A reasonable synthetic route to the required 2,2'-di-iododiphenylacetylene(167) was devised, starting from the readily

available o-iodobenzoic acid(170). This acid (170) was converted into the methyl ester (171), which on reduction with lithium aluminium hydride gave o-iodobenzyl alcohol(172). Oxidation of this alcohol (172) with manganese dioxide[106] in benzene gave o-iodobenzaldehyde (173). It was hoped that a simple benzoin condensation of (173) to (174), followed by the same sequence of steps already mentioned in the first approach to (52), via the dialdehyde (126), would lead to the desired compound (167). However, this benzoin reaction could not be induced to take place, and although other schemes for the preparation of this simple di-iododiphenylacetylene(167) were available, this line was abandoned, since it was also felt that the known low solubility of the cuprous salt (168), might also hinder the desired reaction.

Attention was therefore turned to the synthesis of the unknown o-iodophenylacetylene(175). It was felt that this compound would be readily prepared from o-iodoacetophenone(176) by the normal method[124], i.e., treatment with phosphorus pentachloride, followed by base dehydrochlorination to yield (175).

Again, the readily available o-iodobenzoic acid(170) was chosen as the starting material. Treatment of this acid (170), with methyllithium, in an attempt to prepare o-iodoacetophenone(176) directly, only gave acetophenone (177) itself. This reaction is apparently similar to treatment of the dibromide (150) with butyllithium, which gives, via the dilithio derivative (149), the parent

hydrocarbon (71), after an aqueous work up[125].

At this time, the synthesis of o-iodophenylacetylene(175) was reported by Bott, Eaborn and Walton[126]. The required compound (175) was prepared according to their procedure[127], i.e., the acid (170) was converted to the acid chloride (178), which was reacted with the magnesiumethoxy salt of diethyl malonate[128], and gave o-iodoacetophenone(176), after hydrolysis and decarboxylation. Treatment of (176) with phosphorus pentachloride, followed by dehydrochlorination with ethanolic potassium hydroxide[124], gave o-iodophenylacetylene(175).

The cuprous salt was prepared in the usual way[129], and heated under reflux for 8 hr. in pyridine in an atmosphere of nitrogen. A crude mixture was obtained, which appeared to contain a high proportion of polymeric material. However, the u.v. spectrum of the crude product (Fig. 5) contained some unusual bands, which were not present in the starting material, and were also shown not to be due to the oxidatively coupled product (179), which was prepared for comparison purposes. (See Section IV). Hydrogenation of the crude product appeared to give the hydrocarbon (162) (~1%) on g.l.c. comparison with an authentic sample. This reaction therefore appears very promising, but lack of time precluded any further work on this approach.

However, the reaction does seem worthy of further investigation, particularly from the point of view of high-dilution experiments,

which should reduce the percentage of polymeric material, and thus increase the yield of the macrocyclic acetylenic hydrocarbon (52).

EXPERIMENTAL. SECTION II.

Preparation of o-xylylenebis(triphenylphosphonium bromide) (112)[92].

A solution of o-xylylene dibromide(111) (6.63gm.) and triphenylphosphine (14.25gm.) in dry dimethylformamide (50ml.) was heated under reflux for 3 hr. The reaction mixture was cooled, and the precipitated salt (112) was filtered, and washed thoroughly with ether. Recrystallisation from chloroform gave o-xylylenebis-(triphenylphosphonium bromide) (112) (17.2gm. - 87%) as prisms, m.p. $> 350^{\circ}$. (Griffin, Martin and Douglas[92] give m.p. $> 340^{\circ}$).

Preparation of 1,2-distyrylbenzene(115)[92].

A solution of o-xylylenebis(triphenylphosphonium bromide) (112) (21.25gm.) and benzaldehyde (113) (6.3gm.) in absolute ethanol (75ml.) was treated with a solution of lithium ethoxide in ethanol (0.4 molar; 250ml.). The solution was allowed to stand at room temperature for 30 min., and was heated under reflux for 2 hr., to yield an orange solution. The ethanolic solution was concentrated under reduced pressure (to ~50ml.) and water (200ml.) was added. The reaction mixture was extracted thoroughly with ether, and the combined ethereal extracts washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a pale yellow oil (21gm.), which was chromatographed on alumina (Brockmann Grade I; 400gm.). Several fractions were eluted with petrol, and each fraction was shown to be a mixture of four compounds by t.l.c.

(silica - petrol as eluent, R_F 0.65, 0.6, 0.32 and 0.3). The total product (6.25gm.) showed u.v. absorption at 285mμ and 305mμ, and i.r. absorption (melted film) at ~960cm.$^{-1}$ (νCH=CH trans) and ~850cm.$^{-1}$ (νCH=CH cis). A portion of the product (800mg.) was chromatographed on silica impregnated with silver nitrate (25%; 50gm.), and four main fractions were eluted with petrol.

(i) Fraction I was obtained as a low-melting solid (~30°) (42mg. - 6%), and was shown to be 2-methyl-cis-stilbene(127). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.65, and the i.r. spectrum (melted film) showed absorption at ~680cm.$^{-1}$ (νCH=CH cis). The u.v. spectrum (hexane) had λmax 263mμ(log ε, 3.96), (see Section III). Mass spectrum: molecular ion at 194, ($C_{15}H_{14}$ requires M.W. 194). The n.m.r. spectrum showed a complex multiplet at ~2.95τ (9 protons), a singlet at 3.32τ (2 protons) and a singlet at 7.72τ (3 protons). (Table 3). Refluxing this compound in solution in benzene containing a trace of iodine, converted it into the trans-isomer (128), identical by i.r., u.v. and t.l.c. with fraction II below.

(ii) Fraction II was obtained as a solid, m.p. 40-42°, (71mg. - 10%), and was shown to be 2-methyl-trans-stilbene(128), (Bergmann and Schapiro[130] give b.p. 120-125°/0.15mm.). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.6, and the i.r. spectrum (melted film) showed absorption at ~980cm.$^{-1}$ (νCH=CH trans). The u.v. spectrum (ethanol) had λmax 295mμ (log ε, 4.33), (see Section III).

Mass spectrum: molecular ion at 194, ($C_{15}H_{14}$ requires M.W. 194). The n.m.r. spectrum consisted of a complex multiplet at ~2.8 τ (11 protons) and a singlet at 7.58 τ (3 protons). (Table 3).

(iii) Fraction III was obtained as a solid, m.p. 74-95°, (370mg. - 38%), and was shown by t.l.c. (silica - petrol as eluent) to be a mixture of two compounds, the major component being the faster-running of the two neighbouring spots of R_F ~ 0.3. The slower-running spot was much less prominent. The major component is thought to be the cis-cis-isomer of 1,2-distyrylbenzene(115). The i.r. spectrum (CS_2 solution) was devoid of absorption between 900cm.$^{-1}$ and 1000cm.$^{-1}$ (νCH=CH trans) and showed absorption at ~700cm.$^{-1}$ (νCH=CH cis). The u.v. spectrum (ethanol) showed broad absorption at 280mμ (log ε, 4.24). The n.m.r. spectrum consisted of a singlet at 2.92 τ (14 protons) and a singlet at 3.43 τ (4 protons). (Table 3). A benzene solution containing iodine was isomerised as before, (see below).

(iv) Fraction IV was obtained as a solid, m.p. 82-99°, (260mg. - 27%). T.l.c. (silica - petrol as eluent) showed two neighbouring spots, R_F 0.3, the slower-running one being the more prominent. The major component is thought to be the cis-trans-isomer of 1,2-distyrylbenzene(115). The i.r. spectrum (CS_2 solution) showed absorption at 956cm.$^{-1}$ (νCH=CH trans) and at ~700cm.$^{-1}$ (νCH=CH cis). The u.v. spectrum (ethanol) showed absorption at 285mμ (log ε, 4.01) and at 305mμ (log ε, 4.17). The n.m.r. spectrum consisted of a complex band centred at ~2.95 τ (14 protons), a singlet at 3.31 τ (2 protons)

and a singlet at 3.44τ (2 protons). (Table 3). Refluxing in benzene containing iodine as before, only appeared to remove the faster-running of the two neighbouring spots on t.l.c., leaving a spot of R_F 0.3. The u.v. spectrum was virtually unchanged: the u.v. spectrum and t.l.c. behaviour of the product from isomerisation of fraction III were identical to those of the product of attempted isomerisation of fraction IV.

Preparation of 2-methylstilbene dibromide(131).

(a) From 2-methyl-trans-stilbene(128). A solution of (128) (210mg.) in chloroform (5ml.) was treated with excess of bromine in solution in chloroform, and the reaction mixture heated under reflux for 30 min. The solvent and excess bromine were removed under reduced pressure, and the resulting solid recrystallised from aqueous ethanol to give the meso-dibromide (131), (324mg. - 84%), as prisms, m.p. 155-156°. (Bergmann and Schapiro[130] give m.p. 158-159°). (Found: C, 50.85; H, 4.10. $C_{15}H_{14}Br_2$ requires C,50.90; H, 4.00%). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.15.

(b) From 2-methyl-cis-stilbene(127). The dl-dibromide (131) was prepared from 2-methyl-cis-stilbene(127) (85mg.) in chloroform as above, and was obtained (125mg. - 79%) as prisms, m.p. 101-103°, from aqueous ethanol. T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.15.

Preparation of 2-methyldiphenylacetylene(132).

(a) From the meso-dibromide (131). The dibromide (131) (80mg.) was added to a solution potassium hydroxide (200mg.) in triethylene glycol (1ml.), and the reaction mixture heated at 160° for 5 min., cooled, and poured into water. The reaction mixture was extracted with ether, and the combined ethereal extracts washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave 2-methyldiphenylacetylene(132), (35mg. - 81%) as an oil b.p. 120°/0.1mm. (block). (Found: C, 92.85; H,5.85. $C_{15}H_{12}$ requires C, 93.70; H, 6.30%). Mass spectrum: molecular ion at 192, ($C_{15}H_{12}$ requires M.W. 192). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.35. The i.r. spectrum (liquid film) showed weak absorption at ~2200cm.$^{-1}$ ($\nu C{\equiv}C$), and the u.v. spectrum(hexane) had λmax 269mμ, 277mμ, 284mμ, 293mμ and 303mμ, (log ε, 4.29, 4.32, 4.41, 4.26 and 4.33, respectively), (see Section III). The n.m.r. spectrum consisted of a complex multiplet centred at ~2.85τ (9 protons) and a singlet at 7.55τ (3 protons).

(b) From the dl-dibromide (131). The dl-dibromide (131) (85mg.) was treated as above, and gave the hydrocarbon (132) (36mg. - 78%), which was identical with the sample prepared above, by i.r., u.v. and t.l.c.

Preparation of 3,4-benzo-1,2,5,6-tetrabromo-1,6-diphenylhex-3-ene(117).

A solution of bromine (12.8gm.) in ether (25ml.) was added dropwise to a cooled solution of the diene (115) (5.70gm.) in ether (25ml.). When addition was complete, the reaction mixture was heated under reflux for 1 hr., and the solvent and excess bromine removed under reduced pressure. The resulting crude solid was crystallised from acetic acid to give the tetrabromide (117) (8.1gm. - 67%), as needles, m.p.171-174°. (Found; C, 43.60; H, 3.05. $C_{22}H_{18}Br_4$ requires C, 43.85; H, 3.00%). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.1.

Preparation of 1,2-bis(β-phenylethynyl)benzene(56).

The tetrabromide (117) (1.21gm.) was added to a solution of potassium hydroxide (0.3gm.) in triethylene glycol (25ml.). The reaction mixture was heated at 160° for 5 min., and worked up as in the previous preparation of the hydrocarbon (132). The hydrocarbon (56) was obtained (0.39gm. - 70%) as needles, m.p. 80-81°, from ethanol. (Found: C, 94.80; H, 5.10. $C_{22}H_{14}$ requires C, 94.95; H, 5.05%). Mass spectrum: molecular ion at 278, ($C_{22}H_{14}$ requires M.W. 278). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.15. The n.m.r. spectrum consisted of a complex multiplet centred at 2.58τ. The i.r. spectrum (nujol mull) showed weak absorption at ~2200cm.$^{-1}$, and the u.v. spectrum (hexane) had λ_{max} 259mμ, 273mμ, and 312mμ (log ε, 4.45, 4.67 and 4.26, respectively)(Fig.3).

Preparation of 1,2-diphenethylbenzene(133).

The diene (115) (245mg.) in ethyl acetate (15ml.) was hydrogenated (5% palladium on charcoal as catalyst) until the uptake of hydrogen ceased, which was close to the theoretical value. The reaction mixture was filtered, and the solvent evaporated to yield (133) (230mg. - 93%) as a clear oil, b.p. 165°/0.2mm. (block). (Found: C, 92.10; H, 7.55. $C_{22}H_{22}$ requires C, 92.25; H, 7.75%). Mass spectrum: molecular ion at 286, ($C_{22}H_{22}$ requires M.W. 286). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.45. G.l.c. (1% S.E.30 on "Gas Chrom P", 100-120 mesh, at 190°) showed only one peak, retention time 6 min. The i.r. spectrum (liquid film) and u.v. spectrum (ethanol) were typical of aromatic hydrocarbons. The n.m.r. spectrum consisted of a doublet at 2.92 τ(14 protons) and a singlet at 7.18 τ(8 protons).

Hydrogenation of 1,2-bis(β-phenylethynyl)benzene(56).

The diyne (56) (45mg.) was hydrogenated as in the previous experiment. Work up in the usual way gave a colourless oil, (46mg. - 98%), which was not purified. It was shown to be identical with the saturated hydrocarbon (133) by i.r., u.v., t.l.c. and g.l.c. T.l.c. and g.l.c. also revealed that no other compounds were present.

Attempted preparation of 1,2-bis(o-methylstyryl)benzene(116)[92].

A solution of the bisphosphonium salt (112) (32gm.) and o-tolualdehyde (114) (10.8gm.) in absolute ethanol (100ml.) was treated with a solution of lithium ethoxide in ethanol (0.4 molar; 400ml.). The reaction mixture was allowed to stand at room temperature for 30 min., and then heated under reflux for 4 hr. Work up as in the preparation of 1,2-distyrylbenzene(115) gave a pale yellow oil which was chromatographed on alumina as before. Elution with petrol, and collection of several fractions, gave several low-melting solids (m.p. ~ 30-50°) (total 6.2gm.), which were shown later, by comparison with authentic samples, to be mainly mixtures of 2,2'-dimethyl-cis-stilbene(134) and 2,2'-dimethyl-trans-stilbene(135). Only a trace (if any) of the expected hydrocarbon (116) appeared to be present.

Preparation of diphthalyl(146)[118].

A mixture of phthalic anhydride(148) (150gm.), phthalide(147) (75gm.) and sodium acetate (35gm.) were heated at 300° for 10 hr. On cooling, the reaction mixture solidified. The crude solid was powdered, and washed thoroughly with hot water and hot ethanol. Recrystallisation from acetic acid gave diphthalyl(146) (47gm. - 34%) as orange needles, m.p. 332° (Graebe and Guye[118] give m.p. 331°). (Found: C, 72.75; H, 3.30. $C_{16}H_8O_4$ requires C, 72.75; H, 3.05%). The i.r. spectrum (KCl disc) showed carbonyl absorption

at 1786cm.$^{-1}$, 1751cm.$^{-1}$ and 1731cm.$^{-1}$ and the u.v. spectrum (acetic acid) had λmax 253mμ, 259mμ, 297mμ, 310mμ, 340mμ, 352mμ and 361mμ, (log ε, 4.14, 4.14, 4.07, 4.16, 4.16, 4.23 and 4.09, respectively).

Zinc/acetamide reduction of diphthalyl(146).

A mixture of diphthalyl(146) (1gm.), zinc (3gm.) and molten acetamide (50ml.) was stirred at 160° for 12 hr., and poured into dilute hydrochloric acid. The resulting precipitate was collected, washed with water and dried. The crude pinkish solid (690mg.) had m.p. 195-210°. This solid, which was slightly soluble in aqueous sodium hydrogen carbonate solution and in aqueous sodium hydroxide solution, was very insoluble in organic solvents, and attempted purification by sublimation and recrystallisation failed. The i.r. spectrum of the solid (KCl disc) was typical of a carboxylic acid and showed carbonyl absorption at~1690cm.$^{-1}$ and broad bonded hydroxyl absorption at ~3000cm.$^{-1}$. The u.v. spectrum (acetic acid) had λmax 320mμ. The mass spectrum showed a molecular ion at 266, which would be correct for (143).

The attempted reduction of (146) with zinc in either (i) acetic acid, (ii) ethanol or (iii) trifluoroacetic acid, gave only unchanged starting material (146).

Attempted esterification of this "acid", using either (a) diazomethane in ether, (b) diazomethane in acetone, (c) methanol/

hydrochloric acid, (d) dimethylsulphate/potassium carbonate/acetone, or (e) methyl iodide/ potassium carbonate/acetone, was unsuccessful. Some ester appeared to be formed on treatment of the "acid" with excess of diazomethane in ether or acetone, i.e., the crude solid obtained on removal of the solvent no longer showed hydroxyl absorption in the i.r. spectrum (nujol mull), and the carbonyl frequency changed to ~1720cm.$^{-1}$. However, this solid could not be recrystallised, and attempted purification by preparative t.l.c. (silica - 10% ethyl acetate as eluent) produced several brightly coloured, high-melting crystalline solids. These intriguing compounds were not further investigated. The mass spectrum of the crude product was uniformative: the only possible parent ions were at 266 and 298, and the expected ions at 280 (mono-ester) and 294 (di-ester) were absent.

Preparation of 1-bromomethyl-2-methylbenzene(154)[121].

Bromine (252gm.) was added dropwise over 2 hr. to o-xylene (153) (150gm.) at 130°. The reaction mixture was heated for a further period of 1 hr., cooled, and the hydrogen bromide removed under reduced pressure. The residual oil was dried (calcium chloride) and distilled to give the bromide (154) (207gm. - 79%) as an oil, b.p. 217-220°. (Atkinson and Thorpe[121] give b.p. 215-218°).

Reaction of benzyl chloride (155) with sodamide in liquid ammonia[100].

A solution of benzyl chloride(155) (2.53gm.) in ether (10ml.) was added dropwise to a suspension of sodamide in liquid ammonia [from sodium (0.5gm.) in ammonia (50ml.)]. The reaction mixture was stirred for 3 hr., more ether (50ml.) was added, and the reaction mixture worked up by the careful addition of water. The ether layer was separated, washed successively with water, dilute sulphuric acid, water, aqueous sodium carbonate solution, and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave trans-stilbene(129) (1.3gm. - 72%) as plates, m.p. 124°, from ethanol. The mixed m.p. with an authentic sample of trans-stilbene was 124°, and the i.r. and u.v. spectra were identical with those of the authentic sample, and t.l.c. (silica - petrol as eluent) of each sample showed only one spot, R_F 0.6.

Reaction of the bromide (154) with sodamide in liquid ammonia.

A solution of the bromide (154) (2.7gm.) in ether (10ml.) was treated with sodamide in liquid ammonia [from sodium (0.5gm.) in ammonia (50ml.)] as in the previous experiment. Work up in the usual way, gave an oil (2.1gm.), which was shown by t.l.c. (silica - petrol as eluent) to be a mixture of several components. The i.r. spectrum (liquid film) showed only weak absorption at ~960cm.$^{-1}$, and was devoid of absorption in the region of 700cm.$^{-1}$.

Preparation of (o-methylbenzyl)triphenylphosphonium bromide(156).

A solution of the bromide(154) (146gm.) and triphenylphosphine (230gm.) in benzene (1500ml.) was heated under reflux for 8 hr., cooled, and the resulting crystalline deposit filtered and washed with benzene and ether. Recrystallisation from chloroform gave the salt (153) (302gm. - 86%) as prisms, m.p. 265°. (Found: Br, 17.93. $C_{26}H_{24}PBr$ requires Br, 17.87%).

Preparation of 2,2'-dimethylstilbene(134 and 135).

A solution of the phosphonium salt (156) (33.5gm.) and o-tolualdehyde (114) (10gm.) in absolute ethanol (200ml.) was treated with lithium ethoxide in ethanol (0.4 molar; 400ml.). The reaction mixture was allowed to stand at room temperature for 30 min., and heated under reflux for 4 hr. The reaction mixture was then worked up as in the preparation of the hydrocarbon (115), to give a yellow oil. This oil was chromatographed on alumina (Brockmann Grade I; 1000gm.) and elution with petrol gave 2,2'-dimethylstilbene (134 and 135) (11.61gm. - 74%) as a solid mixture of cis- and trans-isomers, m.p. 38-43°. T.l.c. (silica - petrol as eluent) showed two neighbouring spots, R_F 0.65 and 0.6. Preparative t.l.c. separated a portion of this mixture (100mg.) into three fractions.

(i) Fraction I was obtained (31mg.) as a solid, m.p. 41-44°, and was shown to be 2,2'-dimethyl-cis-stilbene(134). Mass spectrum: molecular ion at 208, ($C_{16}H_{16}$ requires M.W. 208). T.l.c. (silica

- petrol as eluent) showed only one spot, R_F 0.65. The i.r. spectrum (melted film) showed absorption at ~700cm.$^{-1}$ (νCH=CH cis), and the u.v. spectrum (ethanol) had λmax 264mμ (log ε, 3.95), (see Section III). The n.m.r. spectrum consisted of a complex multiplet at 2.98τ (8 protons), a singlet at 3.30τ (2 protons) and a singlet at 7.74τ (6 protons). (Table 3).

(ii) Fraction II was still a mixture of the two spots, (25mg.).

(iii) Fraction III was obtained (40mg.) as a solid, m.p. 79-81°, and was shown to be 2,2'-dimethyl-trans-stilbene(135). (Späth[131] gives m.p. 83°). Mass spectrum: molecular ion at 208, ($C_{16}H_{16}$ requires M.W. 208). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.6. The i.r. spectrum (melted film) showed absorption at ~960cm.$^{-1}$ (νCH=CH trans), and the u.v. spectrum (ethanol) had λmax 293mμ (log ε, 4.38), (see Section III). The n.m.r. spectrum consisted of a complex multiplet centred at ~2.6τ (10 protons) and a singlet at 7.58τ (6 protons). (Table 3).

Preparation of 2,2'-dimethylstilbene dibromide(157).

A solution of bromine (1.6gm.) in acetic acid (10ml.) was added to a solution of the hydrocarbon (134 and 135) (2.08gm.) in acetic acid (30ml.), and the reaction mixture heated under reflux for 1 min. The reaction mixture was cooled, and the precipitated crystals of the dibromide(157) were collected, washed with water, and dried. Recrystallisation from acetic acid gave the dibromide

(157) (2.9gm. - 79%) as prisms, m.p. 166-173°. (Found: C, 52.30; H, 4.40. $C_{16}H_{16}Br_2$ requires C, 52.20; H, 4.40%). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.15.

Preparation of 2,2'-dimethyldiphenylacetylene(158).

The dibromide(157) (2gm.) was added to a solution of potassium hydroxide (1gm.) in triethylene glycol (10ml.) and the reaction mixture heated at 160° for 5 min., cooled, poured into water and extracted with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a yellow oil (1.1gm.) which was chromatographed on silica impregnated with silver nitrate (25%; 50gm.). Elution with petrol gave the hydrocarbon (158) (0.93gm. - 87%) as needles, m.p. 27-28°. (Coops, Hoijtink, Kramer and Faber[132], give m.p. 28.7°). Mass spectrum: molecular ion at 206, ($C_{16}H_{14}$ requires M.W. 206). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.65. The i.r. spectrum (melted film) showed weak absorption at ~2150cm.$^{-1}$ and the u.v. spectrum (ethanol) had λmax 270mμ, 277mμ, 284mμ, 294mμ and 304mμ, (log ε, 4.23, 4.28, 4.39, 4.24 and 4.34, respectively), (see Section III).

In some of the larger scale experiments, 2,2'-dimethyl-*trans*-stilbene(135) [characterised by its mass spectrum, i.r. and u.v. absorption and t.l.c. behaviour] was also isolated (in varying yields) from this reaction. In order to investigate this reaction further,

several dibromides were treated with different reagents under varying conditions. These reactions were worked up as before, and examined by t.l.c. and u.v. spectroscopy. The conditions and results are summarised in Table 4.

Preparation of 1,2-dibromomethyldiphenylacetylene(160).

1,2-Dimethyldiphenylacetylene(158) (415mg.), N-bromosuccinimide (715mg.) and dibenzoylperoxide (10mg.) in dry carbon tetrachloride (5ml.) were heated under reflux for 18 hr. The reaction mixture was cooled, and filtered from the precipitated succinimide. Evaporation of the solvent from the filtrate gave a crude solid which was chromatographed on silica (30gm.). Elution with carbon tetrachloride-petrol (20%) gave the mono-bromide (159) (130mg.- 28%) as needles, m.p. 63-65° from pentane. Mass spectrum: molecular ions at 284 and 286 (ratio 1:1), ($C_{16}H_{13}Br$ requires M.W. 285). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.25, and the u.v. spectrum (ethanol) had λmax 288mμ and 304mμ (log ε, 4.04 and 3.98, respectively), (see Section III).

Elution with carbon tetrachloride gave the dibromide (160) (410mg. - 56%) as needles, m.p. 126-127° from acetic acid. (Found: C, 52.70; H, 3.40. $C_{15}H_{12}Br_2$ requires C, 52.80; H, 3.30%). Mass spectrum: molecular ions at 362, 364 and 366, (ratio 1:2:1), ($C_{16}H_{12}Br_2$ requires M.W. 364). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.15. The u.v. spectrum (ethanol) had λmax

292mμ and 312mμ (log ε, 4.17 and 4.05, respectively) (see Section III), and the n.m.r. spectrum consisted of a complex multiplet centred at 2.63τ (8 protons) and a singlet at 5.2τ (4 protons).

Preparation of 2,2'-bis(triphenylphosphoniummethyl)diphenylacetylene dibromide(142).

A solution of the dibromide (160) (3.89gm.) and triphenylphosphine (5.62gm.) in dry dimethylformamide (15ml.) was heated at 110° for 3 hr. The reaction mixture was cooled, and the diphosphonium salt (142) (9.46gm. - 100%) was collected, washed with ether and dried. Recrystallisation from chloroform gave (142) as prisms, m.p. 326-347°. (Found: Br, 17.70. $C_{52}H_{42}P_2Br_2$ requires Br, 18.00%). T.l.c. (silica - petrol as eluent) showed only one spot on the origin.

The mono-phosphonium salt (161) was also prepared as follows. A solution of the dibromide (160) (61mg.) and triphenylphosphine (44mg.) in benzene (1ml.) was heated under reflux for 3 hr. The reaction mixture was cooled, and the precipitated monophosphonium salt (161) (86mg. - 82%), as prisms, m.p. 220-230°, was collected, washed with benzene and dried. T.l.c. (silica - petrol as eluent) showed one spot, just removed from the origin, R_F 0.05.

Condensation of 2,2'-bis(triphenylphosphoniummethyl)diphenylacetylene dibromide(142) with o-phthaldialdehyde(136).

A mixture of the bisphosphonium salt (142) (1gm.) and o-phthal-

dialdehyde(136) (150mg.) in absolute ethanol (20ml.) was treated with lithium ethoxide in ethanol (0.2 molar; 2ml.) and the reaction mixture heated under reflux for 24 hr. The ethanol was removed under reduced pressure and the resulting crude solid extracted thoroughly with hot petrol to give a solid (358mg.), m.p. 140-306°. (Found: C, 91.45 ; H, 5.85%). The i.r. spectrum (melted film) showed strong absorption at ~970cm.$^{-1}$ (νCH=CH trans) and ~760cm.$^{-1}$, (typical of a 1,2-di-substituted aromatic ring), and the u.v. spectrum (ethanol) showed broad absorption at ~280mμ. The solid was not very soluble in organic solvents, and all attempts at recrystallisation failed. T.l.c. (silica - petrol as eluent) showed, in addition to a small spot at the origin (shown to be due to triphenylphosphine oxide, by running plates in ethyl acetate), at least three closely-running spots, R_F 0.2, 0.15 and 0.1. G.l.c. (1% S.E. 30 on "Gas Chrom P", 100-120 mesh, at 190°) showed 3 peaks of retention times 7 min. (~90%), 26 min. (~5%) and 45 min. (~5%). Sublimation (at 200°/0.1 mm.) only separated the hydrocarbons from the triphenylphosphine oxide, the t.l.c. behaviour after sublimation being almost identical to that before sublimation. Attempted separation of the mixture by column chromatography (silica and alumina) and preparative t.l.c. (silica) was not successful, mixtures of compounds always being obtained. Attempted isomerisation of the mixture by refluxing a chloroform solution containing a trace of iodine was unsuccessful, the mixture being

recovered completely unchanged, even after a 12 hr. reflux.

A portion of the hydrocarbon mixture was hydrogenated (5% palladium on charcoal as catalyst, in ethyl acetate), and the product analysed by g.l.c. (1% S.E. 30 on "Gas Chrom P", 100-120 mesh, at 190°). Three peaks were observed, retention times 6 min. (~5%), 12 min. (~90%) and 28 min. (~5%). The peak of retention time 28 min. was shown to be due to the hydrocarbon (162), by comparison with an authentic sample of (162).

The mixture of compounds was analysed using the technique of t.l.c. combined with mass spectrometry. The fraction corresponding to the spot on t.l.c. of R_F 0.2 gave rise to a molecular ion at 304. The fraction corresponding to the spot of R_F 0.15 gave rise to a molecular ion at 334, the fraction corresponding to the spot of R_F 0.1, giving rise to a molecular ion at 322.

In some of the earlier condensation experiments, the hydrocarbon (158) was isolated, (~5%), identified by i.r. u.v. and t.l.c. comparison with an authentic sample, and by mass spectrometry; molecular ion at 206, ($C_{16}H_{14}$ requires M.W. 206).

Treatment of the mixture with bromine.

A solution of the hydrocarbon mixture in chloroform was refluxed for 2 hr. with an excess of bromine. The solvent was evaporated under reduced pressure, to yield a solid, which was recrystallised with difficulty from acetone, to give needles, m.p. 200-340°. (Found: C, 53.70; H, 3.30%). T.l.c. (silica - carbon tetrachloride

as eluent) showed two spots, R_F 0.7 and 0.6. The crude solid was shown to contain halogen; (Beilstein test and sodium fusion test positive). The u.v. spectrum (ethanol) was transparent above 240mμ. Attempted dehydrobromination using either (i) potassium t-butoxide in benzene, (ii) potassium t-butoxide in t-butanol, (iii) potassium hydroxide in triethylene glycol or (iv) sodamide in liquid ammonia, and examination of the crude product by u.v. spectroscopy, did not produce any compounds showing any unusual bands in the u.v. spectrum.

Reaction of o-xylylene dibromide(111) with sodium in dioxan[122].

A solution of o-xylylene dibromide(111) (35gm.) in dry dioxan (100ml.) was added to powdered sodium (7gm.) in dioxan (400ml.) and the reaction mixture heated under reflux for 48 hr. The dioxan was distilled from the reaction mixture, toluene (200ml.) being added dropwise as a chaser solvent. Benzene (200ml.) and then ethanol (50ml.) was added to the cooled residue, and finally water (300ml.) was carefully added. The organic layer was separated, washed thoroughly with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave an oil, which was chromatographed on alumina (Brockmann Grade I; 400gm.). Elution with petrol gave a colourless solid (3.3gm.), m.p. 98-182°, which was shown by t.l.c. (silica - petrol as eluent) to be a mixture of three compounds, R_F 0.75, 0.72 and 0.55. The three compounds were separated and purified by sublimation and crystallisation.

(i) Fraction I sublimed at 90°/0.1 mm. Recrystallisation from ethanol gave 1,2-dimethyldibenzyl(164), (125mg. - 1%), m.p. 57-58°. (Cope and Fenton[122] give m.p. 56-58°). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.75, and g.l.c. (1% S.E. 30 on "Gas Chrom P", 100-120 mesh, at 125°) showed only one peak, retention time 7 min.

(ii) Fraction II sublimed at 130°/0.1 mm., and recrystallisation from ethanol gave the hydrocarbon (163) (4.95gm. - 36%) as prisms, m.p. 108-109°. (Cope and Fenton[122] give m.p. 109-110°). T.l.c. (silica - petrol as eluent) showed one spot, R_F 0.72, and g.l.c. (1% S.E. 30 on "Gas Chrom P", 100-120 mesh, at 125°) showed only one peak, retention time 9 min.)

(iii) Fraction III sublimed at 220°/0.1mm., and recrystallisation from ethanol gave the hydrocarbon (162) (735mg. - 5%) as needles, m.p. 182-183°. (Cope and Fenton[122] give m.p. 183.5-184.5°). T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.55, and g.l.c. (1% S.E. 30 on "Gas Chrom P" 100-120 mesh at 190°) showed only one peak, retention time 28 min.

Preparation of methyl o-iodobenzoate(171).

A solution of o-iodobenzoic acid(170) (20gm.) in methanol (40ml.) and concentrated sulphuric acid (3ml.) was heated under reflux for 2 hr. The reaction mixture was cooled, poured into water, and extracted thoroughly with ether. The combined ethereal extracts

were washed with water, and extracted with aqueous sodium carbonate solution. [Acidification of the sodium carbonate extract gave unchanged acid (170) (1.8gm. - 9%)]. The ether extract was then washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave the ester (171) (17.8gm. - 85%) as a colourless oil, b.p. 145-146°/14mm. (Heilbron and Bunbury[133], give b.p. 145-146°/16mm.). The i.r. spectrum (liquid film) showed absorption at ~1740cm.$^{-1}$, (νC=O), typical of an ester grouping, and was devoid of any characteristic carboxylic acid absorption bands.

Preparation of o-iodobenzylalcohol(172).

A solution of the ester (171) (18gm.) in anhydrous ether (100ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (2.3gm.) in anhydrous ether (100ml.). The reaction mixture was then heated under reflux for 1 hr., cooled, and the complex carefully destroyed by the addition of a saturated aqueous solution of ammonium sulphate. The ether layer was separated, and the aqueous layer was extracted thoroughly with ether. The combined ethereal extracts were washed with a little water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave the alcohol (172) (13.1gm. - 92%) as needles, m.p. 89.5-90° from water. (Olivier[134] gives m.p. 88.5-90°). The i.r. spectrum (nujol mull) showed absorption at ~3300cm.$^{-1}$ (νOH) and was devoid of absorption in the carbonyl region (~1700cm.$^{-1}$). The i.r. spectrum in carbon tetrachloride

solution, showed interesting intra-molecular hydrogen bonding, (see Section III).

Preparation of o-iodobenzaldehyde(173).

A solution of the alcohol (172) (1gm.) in dry benzene (50ml.), and manganese dioxide (10gm.), were stirred and heated under reflux with automatic water separation. When the separation of water ceased, the reaction mixture was cooled and filtered. Evaporation of the benzene gave an oil, which was purified by steam distillation to give o-iodobenzaldehyde(173) (0.7gm. - 71%), as prisms m.p. 37°. (Rapson and Shuttleworth[135] give m.p. 37°). The i.r. spectrum (nujol mull) showed strong absorption at ~1680cm.$^{-1}$ (νC=O), and was devoid of absorption in the region of 3300cm.$^{-1}$ (νOH).

Attempted preparation of 2,2'-di-iodobenzoin(174).

A solution of o-iodobenzaldehyde(173) (580mg.) and sodium cyanide (25mg.) in aqueous ethanol (50%; 5ml.) was heated under reflux for 6 hr. The reaction mixture was cooled, poured into water, and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave an oil (490mg.) whose i.r. spectrum (liquid film) was identical to that of the starting aldehyde (173).

Reaction of o-iodobenzoic acid(170) with methyllithium.

A solution of o-iodobenzoic acid(170) (2.48gm.) in ether (25ml.) was treated with ethereal methyllithium (0.4 molar; 100ml.), and the reaction mixture heated under reflux for 2 hr. The reaction mixture was worked up by the careful addition of water, and the ether layer separated. [Acidification of the basic aqueous layer gave a solid, (110mg.), m.p. 87° from water, whose i r. spectrum (nujol mull) indicated the presence of a carboxylic acid function. This acidic material was not very soluble in aqueous sodium hydrogen carbonate solution]. The ether layer was washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave an oil, b.p. 87-88°/14mm. which was shown to be acetophenone(177) (0.99gm. - 82%), by comparison of its i.r. spectrum with an authentic sample, and its mass spectrum: molecular ion at 120, (C_8H_8O requires M.W. 120). The 2,4-dinitrophenylhydrazone derivative, did not depress the m.p. of an authentic sample.

Preparation of o-iodoacetophenone(176).

Magnesium (540mg.) was added to absolute ethanol (1ml.) and carbon tetrachloride (0.1ml.), and when the reaction was well under way, anhydrous ether (10ml.) was added. A solution of diethyl-malonate (3.52gm.) in absolute ethanol (5ml.) and anhydrous ether (5ml.) was added dropwise, and the reaction mixture heated under reflux for 3 hr. To the clear solution, o-iodobenzoylchloride(178)

(5.32gm.) [prepared in the usual way[136] from the acid (170) (4.96gm.) and thionyl chloride]in anhydrous ether (10ml.) was added with stirring, and the reaction mixture heated under reflux for 30 min. The reaction mixture was cooled, poured into dilute sulphuric acid, and the ether layer separated, washed with water and the solvent evaporated. A solution of glacial acetic acid (1ml.) and concentrated sulphuric acid (1ml.) in water (5ml.) was added to the crude diethyl acylmalonate, and the reaction mixture heated under reflux until the evolution of carbon dioxide ceased (~2 hr.). The reaction mixture was cooled, poured into aqueous sodium hydroxide solution, and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave o-iodoacetophenone(176) (3.8gm. - 77%) as an oil, b.p. 140-145°/14mm. (Auwers, Lechner and Bundesmann[137] give b.p. 139-140°/12mm.). The i.r. spectrum (liquid film) showed typical aromatic carbonyl absorption at ~1690cm.$^{-1}$.

Preparation of o-iodophenylacetylene(175).

Phosphorus pentachloride (225mg.) was added in portions to o-iodoacetophenone(176) (225mg.). The reaction mixture was allowed to stand at room temperature for 30 min., and the excess phosphorus pentachloride and phosphorus oxychloride were removed under reduced pressure. The i.r. spectrum (liquid film) of the crude residual oil (310mg.) was devoid of absorption in the carbonyl region

(~1700cm.$^{-1}$). The crude mixture was not purified. A solution of potassium hydroxide (150mg.) in ethanol (5ml.) was added to this mixture and the reaction mixture heated under reflux for 6 hr., cooled, and poured into water. The reaction mixture was extracted with ether, and the combined ethereal extracts washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave o-iodophenylacetylene(175) (118mg. - 57%) as an oil, b.p. 70-74°/1mm. (block), n_D^{22} 1.6365. (Bott, Eaborn and Walton[126] give b.p. 75°/1mm., n_D^{25} 1.6362). The i.r. spectrum showed strong absorption at~3300cm.$^{-1}$ (ν≡C-H) and weak absorption at ~2100cm.$^{-1}$ (νC≡C) and was virtually identical to that of an authentic sample provided by Walton[127]. The u.v. spectrum (ethanol) had λmax 243mμ and 248mμ (log ε, 4.31 and 4.30, respectively).

Reaction of cuprous phenylacetylide(135) and iodobenzene(163) in pyridine[123].

A mixture of cuprous phenylacetylide(135) (1.1gm.) [prepared in the usual way[129] from phenylacetylene (77) (0.65gm.) and ammoniacal cuprous chloride[138]] and iodobenzene (163) (1.36gm.) in dry pyridine (65ml.) [which had previously been distilled with a nitrogen bleeder] were heated under reflux in a nitrogen atmosphere for 6 hr. The reaction mixture was cooled, poured into dilute sulphuric acid and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium

sulphate) and filtered. Evaporation of the solvent gave a yellow oil (1.11gm.) which was shown by t.l.c. (silica - petrol as eluent) to be mainly a mixture of diphenylacetylene(71) and diphenyldiacetylene(75). The diphenyldiacetylene(75) was estimated to be present in about 5% from the u.v. spectrum (see Section I).

Reaction of cuprous o-iodophenylacetylide(169) in pyridine.

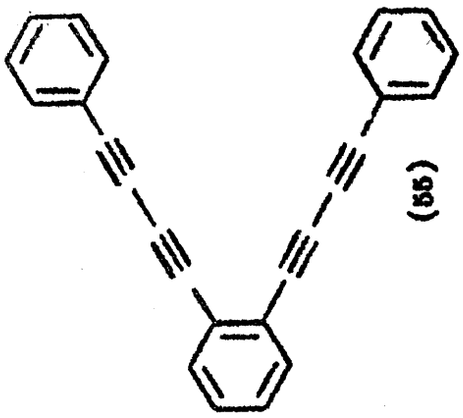
Cuprous o-iodophenylacetylide(169) (2.1gm.) [prepared in the usual way[129] from o-iodophenylacetylene(175) (1.71gm.) and ammoniacal cuprous chloride[133]] in dry pyridine (which had previously been distilled in a nitrogen bleeder) was heated under reflux for 8 hr. in a nitrogen atmosphere. The reaction mixture was cooled, poured into into dilute sulphuric acid, and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a yellow semi-solid (1.1gm.), which was shown by t.l.c. (silica - petrol as eluent) to contain at least six closely-running compounds. The i.r. spectrum (melted film) showed weak absorption at ~2200cm.$^{-1}$ and weak absorption at ~3300cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 256mμ, 264mμ, 271mμ, 278mμ and 287mμ. (Fig. 5).

A portion of the crude product was hydrogenated in ethyl acetate (5% palladium on charcoal as catalyst), and the hydrogenated product analysed by g.l.c. (1% S.E.30 on "Gas Chrom P", 100-120 mesh, at

200°). Several peaks were present, one of which (~1%) appeared to be identical with an authentic sample of the hydrocarbon (162).

Oxidative coupling of o-iodophenylacetylene(175).

A solution of o-iodophenylacetylene(175) (395mg.) and anhydrous cupric acetate (400mg.) in pyridine (10ml.) and methanol (10ml.) was heated under reflux for 2 hr., cooled, poured into dilute sulphuric acid, and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave (179) (375mg. - 95%) as prisms, m.p. 115-116° from ethanol. (Found: C, 42.55; H, 2.10. $C_{16}H_8I_2$ requires C, 42.30; H, 1.80%). T.l.c. (silica - petrol as eluent) gave one spot, R_F 0.4. The i.r. spectrum (melted film) showed weak absorption at ~2200cm.$^{-1}$ and the u.v. spectrum (ethanol) had λmax 299mμ, 318mμ and 339mμ, (log ε, 4.39, 4.72 and 4.68, respectively).



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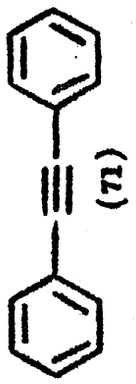

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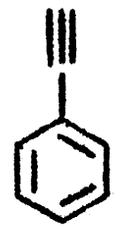

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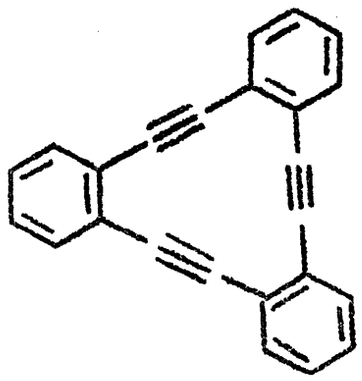

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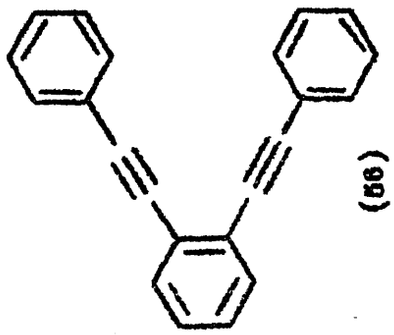

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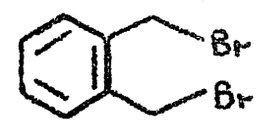

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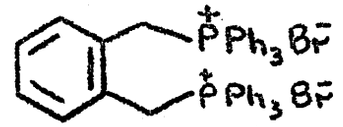

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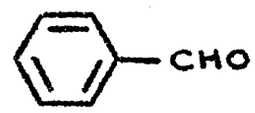

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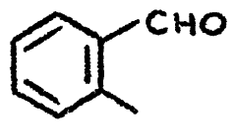

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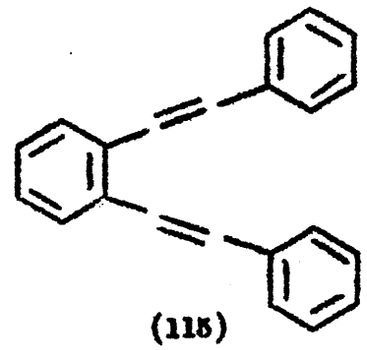

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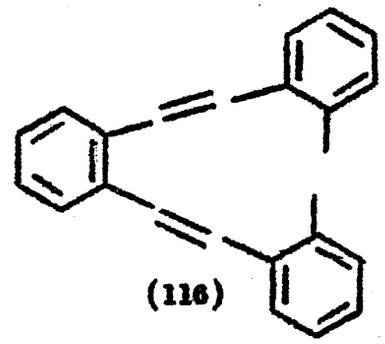

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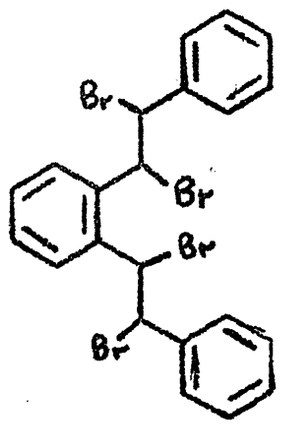

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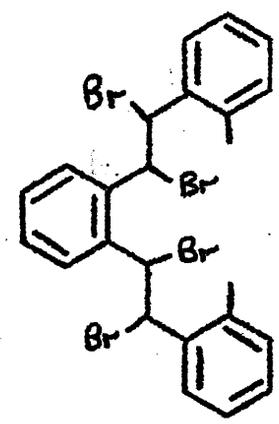

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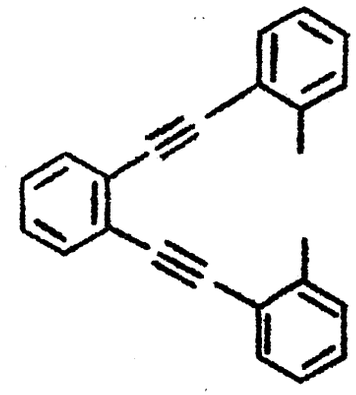

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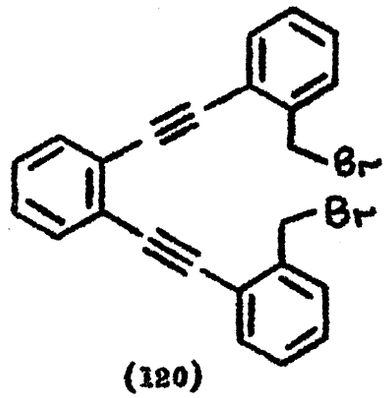

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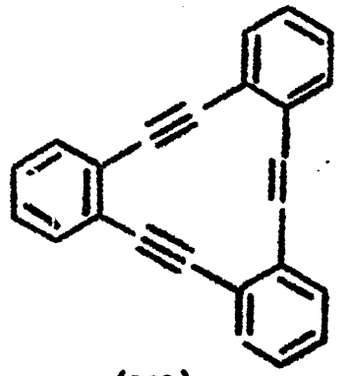

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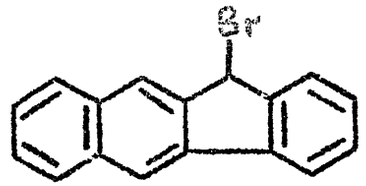

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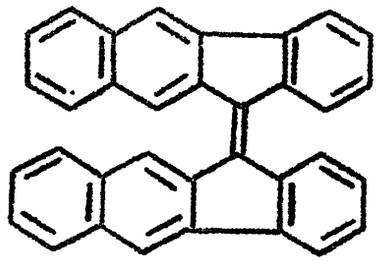

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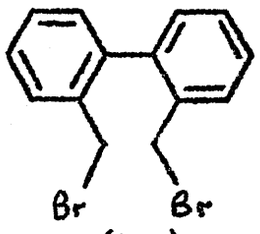

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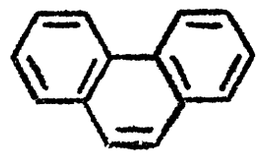

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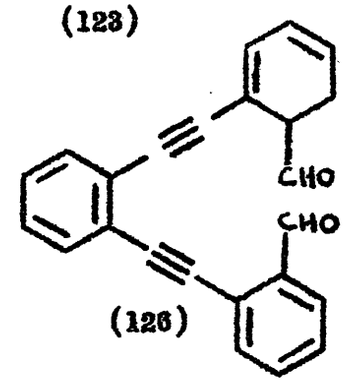

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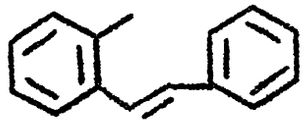

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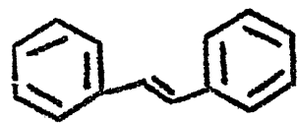

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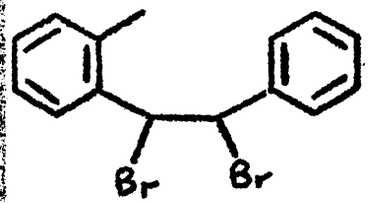

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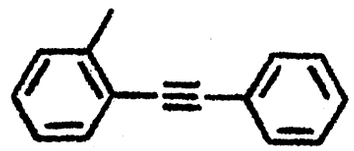

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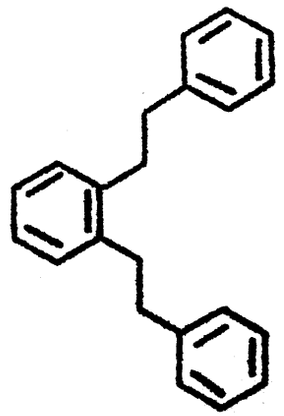

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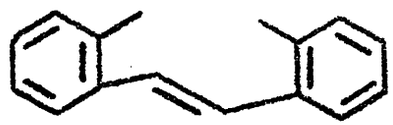

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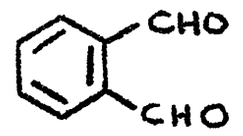

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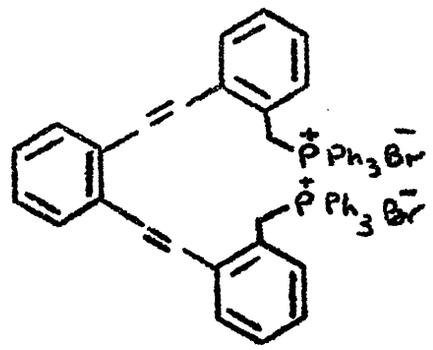

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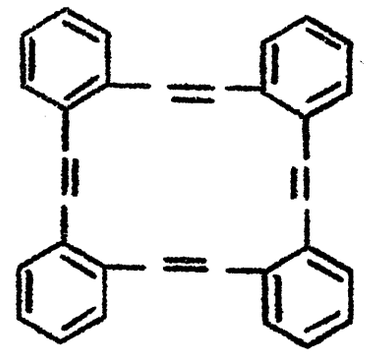

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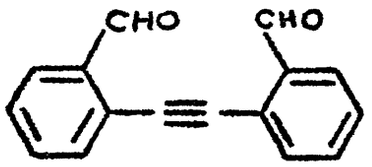

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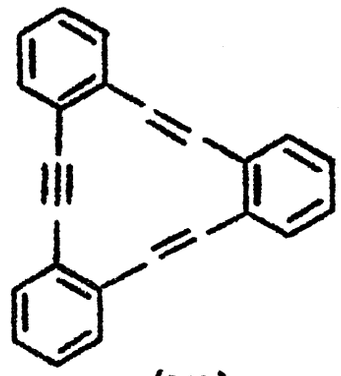

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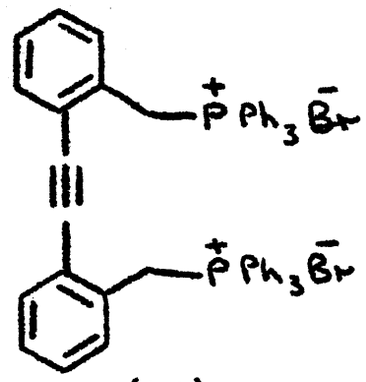

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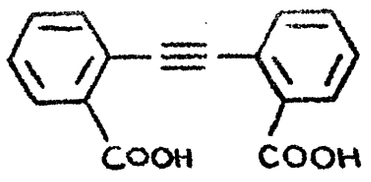

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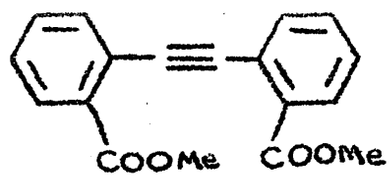

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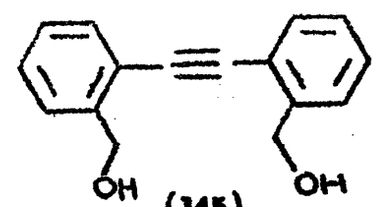

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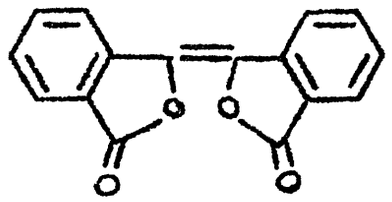

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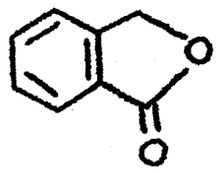

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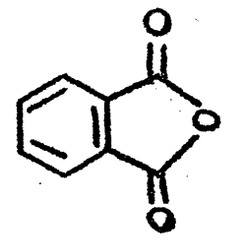

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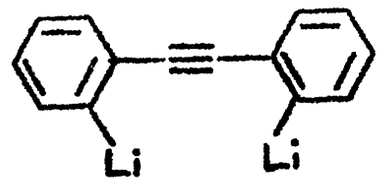

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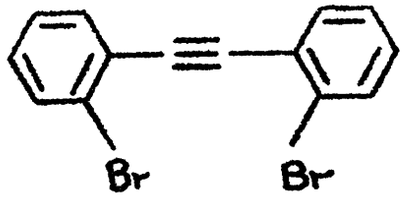

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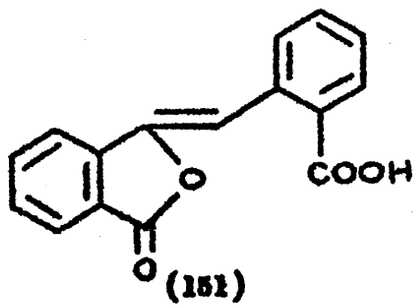

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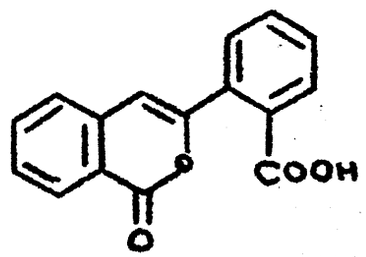

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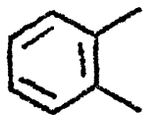

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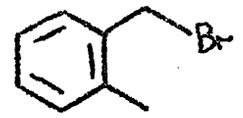

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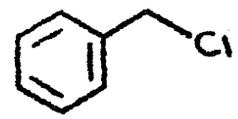

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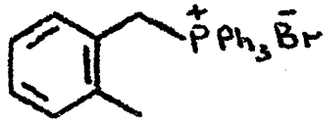

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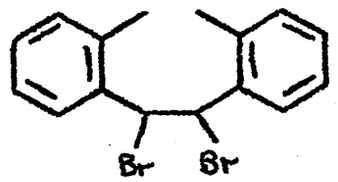

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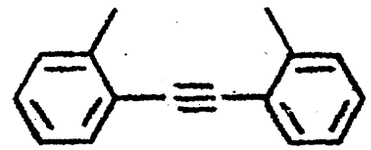

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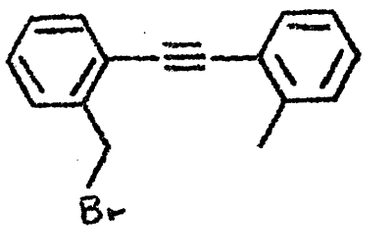

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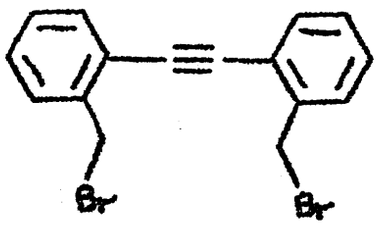

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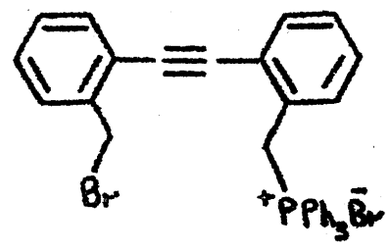

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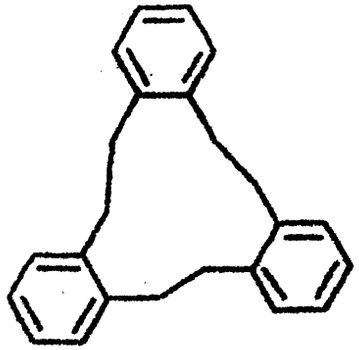

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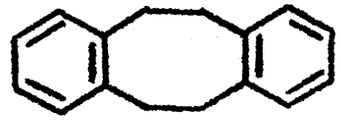

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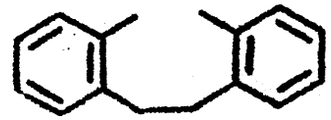

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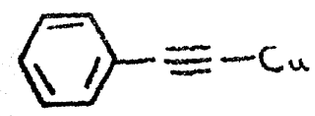

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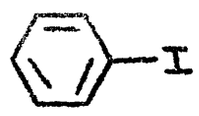

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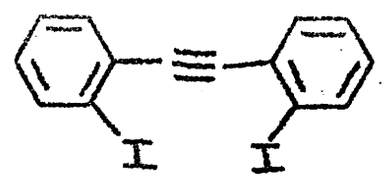

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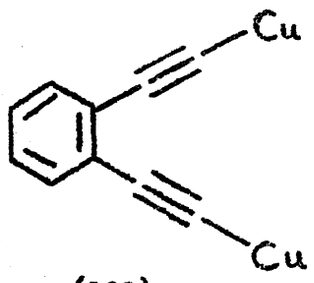

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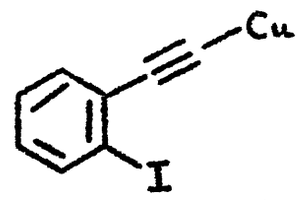

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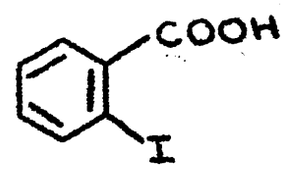

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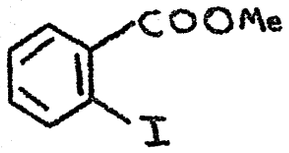

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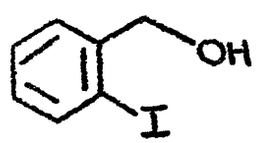

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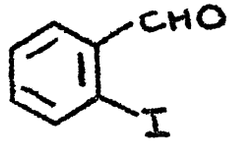

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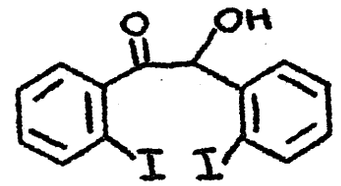

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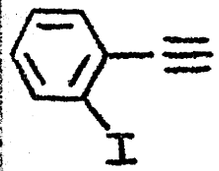

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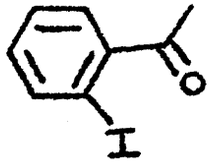

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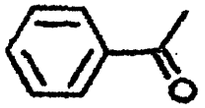

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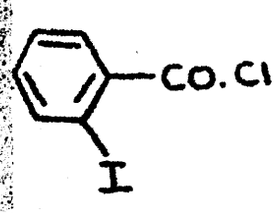

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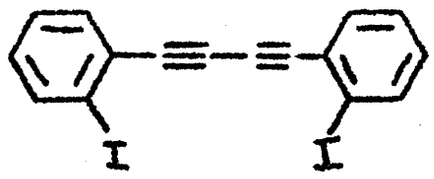

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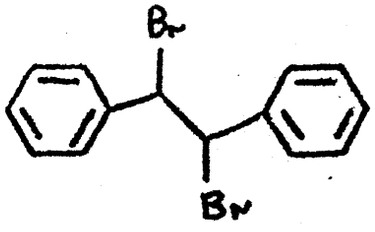

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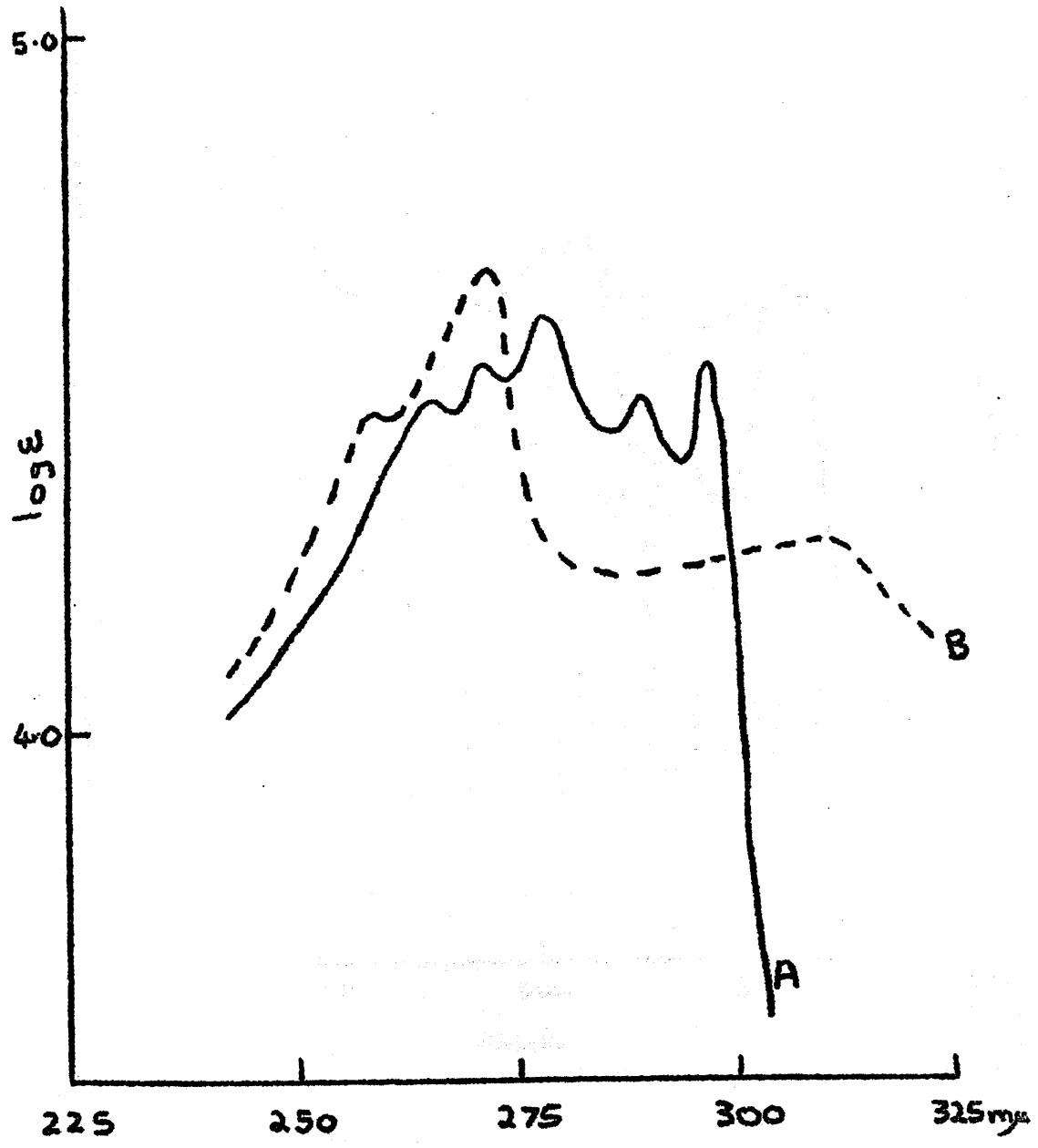


Fig.3.

U.v. spectra:-
A, (71) in ethanol,
B, (56) in hexane.

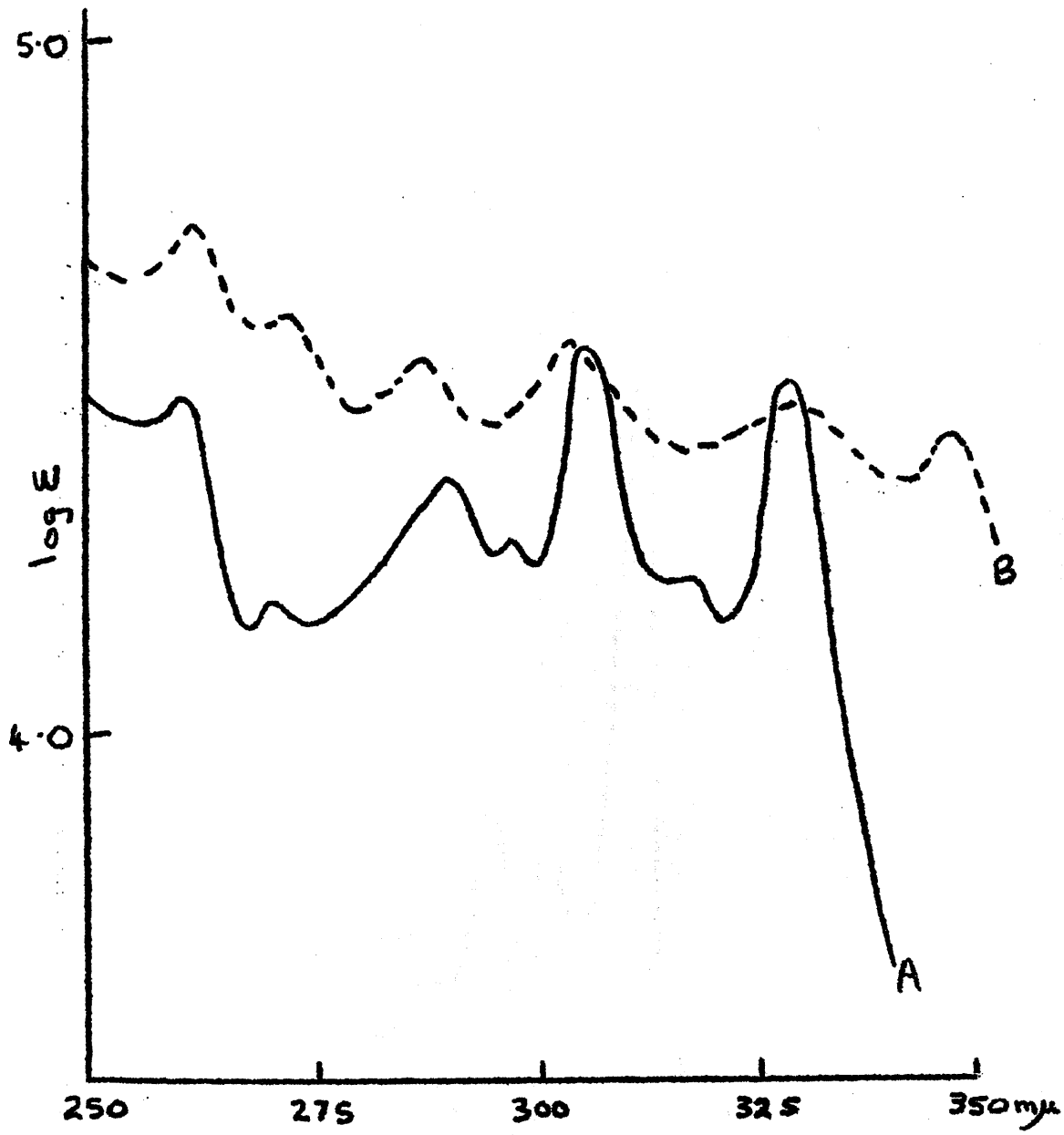


Fig.4.

U.v. spectra:-
A, (75) in ethanol,
B, (55) in cyclohexane[1].

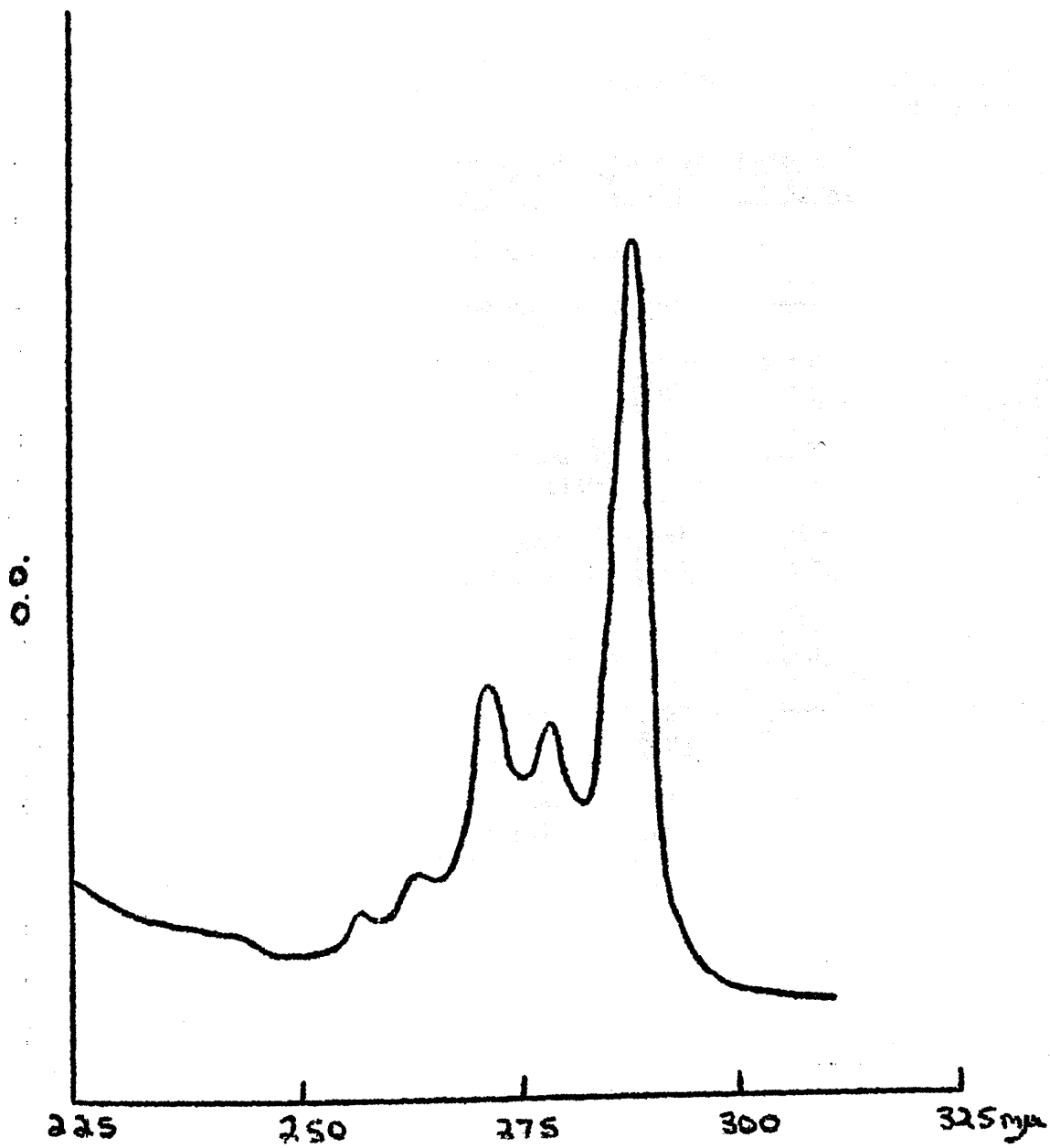


Fig.5.

U.v. spectrum (ethanol) of the crude product obtained from reaction of (169) in pyridine.

TABLE 3 – N.M.R. OF SOME cis- AND trans-STILBENES.

Compound.	Configuration.	τ-values.			Literature Reference.
		Aromatic Protons.	Olefinic Protons.	Methyl Protons.	
(130)	cis	2.82*	3.45*	—	112
(129)	trans	~2.6†	2.90*	—	112
(127)	cis	~2.95† (9H)	3.32* (2H)	7.72* (3H)	—
(128)	trans	~2.8† (11H)		7.58* (3H)	—
(134)	cis	~2.98† (8H)	3.30* (2H)	7.74* (6H)	—
(135)	trans	~2.3† (10H)		7.58* (6H)	—
(115)	cis-cis	2.92* (14H)	3.43* (4H)	—	—
(115)	cis-trans	~2.95† (14H)	3.31* (2H) 3.44* (2H)	—	—

* singlet

† multiplet

Figures in parentheses are integrated values, indicating the number of protons.

TABLE 4 - Br_2 AND HBr ELIMINATIONS.

Compound.	Conditions.	Products.
(180), meso*	T.E.G., 160°, 5 min.	(130), ~5%.
(180), meso*	T.E.G., 200°, 15 min.	(130), ~40%.
(157), meso†	T.E.G., 160°, 5 min.	(134), ~40%.
(157), meso†	Diglyme, 160°, 5 min.	(134), ~35%.
(157), d, l, meso	T.E.G., 160°, 5 min.	(134), ~30%, (135), ~70%.
(157), d, l, meso	Diglyme, 160°, 5 min.	(134), ~25%, (135), ~75%.
(157), meso†	KOH/T.E.G.[a], 160°, 5 min.	(158), ~75%.
(157), meso†	KOH/T.E.G.[b], 160°, 5 min.	(158), ~75%.
(157), d, l, meso	KOH/T.E.G.[a], 160°, 5 min.	(158), ~70%, (135), ~10%.
(157), d, l, meso	KOH/T.E.G.[b], 160°, 5 min.	(158), ~80%.

* Prepared from trans-stilbene(129) in the usual way[139].

† Prepared from (135) as before, m.p.177°.

T.E.G. is triethylene glycol.

[a] KOH not in solution when dibromide added.

[b] KOH in solution when dibromide added.

SECTION III

REACTIONS AND PHYSICAL PROPERTIES OF 2,2'-DIBROMOMETHYLDIPHENYLACETYLENE AND RELATED COMPOUNDS.

The synthesis described in Section II led to 2,2'-dibromomethyldiphenylacetylene(160). This difunctional compound is available in good yield in six stages from o-xylene (153), and is therefore attractive for the synthesis of acetylenic macrocycles and related systems. It is also attractive on the basis of its rigidity, which assists in the formation of cyclic systems (see Section II), and on the basis of the relative disposition of its reactive benzylic bromine atoms. In this section, the dibromide (160) has been used as the starting point for the attempted syntheses of a number of potentially interesting macrocycles, (181, 182, 183, 184, 185 and 186). These experiments unfortunately met with only limited success, and it was not possible to attempt the projected synthesis of two other interesting systems (187, 188). However, the dibromide (160) and derived acyclic derivatives and related systems have been turned to good account in a study of their u.v. and i.r. spectral characteristics. An initial observation of the anomalous u.v. absorption of the dibromide (160) has now been related to a general property of benzylic bromides, and the hydroxyl stretching absorption in the i.r., and u.v. absorption curve, for the corresponding diol (145), have been compared and contrasted with the absorption data for a wide range of derived and related diols, mono-ols and model compounds.

Attempted Syntheses of Certain Macrocycles from 2,2'-Dibromomethyldiphenylacetylene(160).

The reactive benzylic bromine atoms of the dibromide (160), when oriented cisoid with respect to one another, are well disposed spatially for a variety of ring closure reactions by insertion of a second difunctional unit, e.g., as already indicated, one can envisage the replacement of the bromines by (a) a sulphur di-anion or equivalent, leading to compound (181), (b) the acetylide di-anion leading to compound (187), or (c) a second dihalide molecule via a Wurtz reaction leading to (184). In the event, none of these attempts has proved successful, but the relevant details of these and of other similar reactions are described below.

The reaction of the dibromide (160) with zinc in acetamide was carried out in the hope of obtaining the dimeric hydrocarbon (184), or perhaps even the monomer (185). From a study of Dreiding models, this compound (185), appears to be too highly strained to make its formation feasible. However, compounds in which the triple bond is "bent" have been prepared, e.g., the highly strained hydrocarbon (38) has been prepared[63] by high-dilution coupling o-diethynylbenzene(39), (see Section I). In the event, the only hydrocarbon isolated from this reaction was 2,2'-dimethyldiphenylacetylene(158) whose properties were identical with those already obtained for this compound, (t.l.c., i.r. and u.v.), (Section II). Further proof of structure (158) was obtained by hydrogenating the

hydrocarbon to the fully reduced 2,2'-dimethyldibenzyl(184) and comparing this on g.l.c. with an authentic sample, obtained as a by-product from the Wurtz self-coupling of o-xylylene dibromide (111)[122], (Section II), when they were shown to be identical.

Baker, McOmie and Warburton[140] have used phenyllithium for this type of condensation, when they successfully self-condensed the dibromide (190) to give the hydrocarbon (191). However, lack of time precluded a study of the reaction of the dibromide (160) with this reagent.

The reaction of 1,4-dichlorobut-2-yne(192) with aqueous ammonium sulphide to give the cyclic disulphide (193) is known[141]. It was felt that treatment of the dibromide (160) with this reagent could lead, in a similar manner to the sulphide (181), and that this sulphide could be oxidised to the sulphoxide (182) and the sulphone (183) to produce an interesting series of compounds. Cava, Deana and Muth[142] have carried out a similar conversion of the tetrabromide (194) into the disulphide (195), using sodium sulphide. However, no compound corresponding to the structure (181) could be isolated from this reaction. The crude solid obtained was shown by a sodium fusion test to contain sulphur, but no halogen (or nitrogen) was present. T.l.c. indicated that there was essentially only one compound formed; this compound ran faster on elution with 20% ethyl acetate - petrol than did the starting dibromide (160), which was completely removed in this reaction. The rest of

the material stayed at the origin of the plate. All attempts at sublimation and recrystallisation of the crude solid failed, as did preparative t.l.c. (Several bands appeared on running a thick plate - this can happen with easily oxidisable materials). The mass spectrum of the crude solid did not throw any light on the nature of this solid, but it did not appear to have the correct molecular weight for (181).

It would seem possible, that condensation of the dibromide (160), as the bis-Wittig salt, with the dialdehyde (189) could give rise to the interesting hydrocarbon (188), or that reaction of the dibromide (160) with dilithium acetylide would produce the hydrocarbon (187). However, lack of time precluded any attempt to prepare either of these interesting compounds.

It was felt that the oxygen analogue of the as yet unobtainable sulphide (181), namely 3,4:7,8-dibenzo-1-oxacyclonona-3,7-diene-5-yne(186), could perhaps be prepared from the diol (145), by making the mono-tosylate ester (196), and treating this ester with the very reactive base, dimsyl sodium[143]. This reagent should generate the anion (197) of the free hydroxyl, which could conceivably attack the carbon bearing the easily expelled tosylate ester and lead to structure (186). The diol (145) was prepared from the dibromide (160) by lithium aluminium hydride reduction of the diacetate (198), formed from the dibromide (160) by heating it under reflux with fused sodium acetate in acetic acid. However,

benzyl tosylates are known to be very reactive and unstable[144,145], and, in fact, attempted preparation of the monotosylate ester (196) by treatment of the diol (145) with 1.15 equivalents of p-toluenesulphonyl chloride in pyridine, followed by the normal isolation procedure (pouring into water and extraction with organic solvent) only regenerated the starting diol (145). Treatment of the diol (145) with acetic anhydride in pyridine, however, did give the diacetate (198) in excellent yield, so one can postulate that it is not lack of reaction of the diol (145), but rather decomposition of the tosylate ester during the work up, which is responsible for the failure of the reaction to produce the monotosylate ester (196).

In a later experiment, the diol (145) was treated with 1.15 equivalents of p-toluenesulphonyl chloride in pyridine, but this time the pyridine was removed under reduced pressure. The i.r. spectrum of the crude solid residue was substantially different from that of p-toluenesulphonyl chloride, so it was assumed that a reaction had taken place. (Note that t.l.c. showed only starting material, so it is likely that the tosylate ester is even hydrolised on a chromatoplate). The crude mixture, assumed to contain some of the monotosylate ester (196), was treated with dimsyl sodium in dimethylsulphoxide in an attempt to prepare the desired cyclic ether (186), but on normal work up, the dihydroxy compound (145) was recovered unchanged. This is rather surprising, since one would expect, if not attack of the anion on the tosylate ester, (or if

the tosylate ester had not been formed), at least attack of the anion on the triple bond, to produce one of the two enol-ethers (199 or 200), since treatment of the mono-ol (201), formed from the mono-bromide (159), (see Section II), via the mono-acetate (202), in exactly the same way as the diol (145), with dimsyl sodium under exactly the same conditions, yielded one or other or both of the enol-ethers (203 or 204).

The Spectral Properties of some o-Substituted and o,o'-Di-substituted Derivatives of Diphenylacetylene, Stilbene (cis and trans) and Dibenzyl.

(a) The u.v. absorption of benzylic bromides.

This section describes what would now appear to be a general finding, that benzylic bromides display a loss of aromatic fine structure in the 250-300mμ region, which none of the other substituent groups examined ($-CH_3$, $-CH_2O.CO.CH_3$, $-CH_2OH$ and $-CH_2Cl$) do to any appreciable extent. This phenomenon was first observed in the case of the dibromide (160) when its spectrum was compared with that of the parent hydrocarbon (158), (Fig. 6). It was felt at first, that this loss of fine structure was due to some steric effect of the dibromide (160). However, the u.v. spectra of the corresponding diacetate (198) and the diol (145) were virtually identical with that of the parent hydrocarbon (158), (Fig. 6). The same effect was observed in the mono-substituted series, although to a slightly lesser extent. The u.v. spectrum of the

monobromide (159) (Fig. 6), which is obtained as a by-product in the preparation of the dibromide (160), (Section II), is much broader than that of the parent hydrocarbon (158), whereas the u.v. spectra of the mono-acetate (202) and mono-ol (201) are again identical with the parent hydrocarbon (158), (Fig. 6). In the simplest situation examined, i.e., the toluene series, (toluene, benzyl acetate, benzyl alcohol, benzyl chloride and benzyl bromide), the u.v. spectra are all similar to one another, again with the exception of the bromide, (Fig. 7). There does not appear to be any correlation of these results discussed in the literature, but it is clear that an explanation is required. Tyler[146] has suggested that it is unlikely that the explanation for the effect involves any interaction of the bromine lone pair electrons with the aromatic ring, since the bromine atom is separated from the ring by a carbon atom. It is known however, that methyl bromide, in the gas phase, absorbs continuously in this region of the spectrum[146], and it may be that the $-CH_2Br$ group, in solution, is also absorbing continuously and is merely swamping the vibrational fine structure of the aromatic ring. It would be expected that benzyl iodide, since gaseous methyl iodide absorbs approximately in the same region as methyl bromide, would have a u.v. spectrum similar to that of benzyl bromide, whereas the u.v. spectrum of benzyl chloride still shows the vibrational fine structure of the aromatic ring, (Fig. 7), although the absorption is enhanced at shorter wavelengths. This

is in keeping with the fact that methyl chloride, in the gas phase, absorbs u.v. radiation at shorter wavelengths than methyl bromide. The effect appears to be independent of the solvent used, though, of course, the spectra show the expected small solvent shift.

(b) An o-substituent effect in the u.v. spectra of diphenylacetylene and stilbene (cis and trans) derivatives.

During the examination of the dibromide (160), an interesting but unrelated effect in the case of mono- and di- ortho-substituted diphenylacetylenes was observed. The u.v. spectrum of 2-methyldiphenylacetylene(132), (Section II), showed a shift of ~6mμ to longer wavelength than that of the unsubstituted diphenylacetylene (71), (Fig. 8). This effect is quite unexceptional, (c.f. the shift to longer wavelength in the u.v. spectrum of toluene relative to benzene). However, introduction of another methyl group into the ortho position of the other benzene ring has virtually no further effect, i.e., the u.v. spectrum of 2,2'-dimethyldiphenylacetylene (158), (Section II), is essentially identical with that of the monomethyl compound (132), (Fig. 8). There are analogies in the literature for this phenomenon; thus, if the u.v. spectrum of p-methoxy-trans-stilbene[147] is compared with that of trans-stilbene(129) itself, there is observed a shift to longer wavelength, whereas the u.v. spectrum of p,p'-dimethoxy-trans-stilbene[148] is very similar to that of the monomethoxy compound, and shows no further shift. The question one must ask is why there is no further shift by the second

methyl or methoxy group. It would appear that steric interactions can be ruled out, since models do not reveal any strong interactions. Also, there seems to be no loss of intensity in the spectra, which generally follows loss of conjugation due to steric hindrance. However, if one considers that one of the excited states of diphenylacetylene(71) is (207), then introduction of a methyl group into an ortho or para position may lead to an excited state of type (208), which is perhaps stabilised by the inductive effect of the methyl group. The methyl group could feed electrons into the electron deficient ring, making its formation easier. Another methyl group in the other ring would not be able to stabilise the electron deficient ring, e.g., (209), hence the second methyl group would have no further effect.

Measurements were extended to the cis- and trans-stilbene series. In the case of cis-stilbene(130), a methyl group in the ortho position produces a shift to shorter wavelength, together with a drop in intensity, but putting another group ortho in the other ring has no further effect, (Fig. 9), i.e., the u.v. absorption curve of 2-methyl-cis-stilbene(127), (Section II), (λmax 263mμ, log ε, 3.96) is almost identical with that of 2,2'-dimethyl-cis-stilbene(134), (Section II), (λmax 264mμ, log ε, 3.95), and both are different from that of cis-stilbene(130), (λmax 278mμ, log ε, 4.07). This apparent anomaly can be expected due to the pronounced steric interactions which are inevitable in cis-stilbenes,

and these interactions apparently more than offset the normal shift to longer wavelength, expected by the introduction of a methyl group into the aromatic ring. In cis-stilbene(130) itself, the molecule cannot be coplanar due to interactions of the aromatic ring hydrogens, hence the u.v. spectrum is shifted to shorter wavelength from that of trans-stilbene(129), together with a corresponding loss of intensity. The situation is further complicated in the di-o-methyl case, since rotation of the rings out of the plane of the double bond, for relief of the aromatic hydrogen interactions, brings into play methyl-double bond and methyl-aromatic ring interactions. Consequently, from examination of models, conformations are hard to predict, but it is clear that the conformations probably require a twisted conformation. It might be thought that the mono-methyl derivative should show less interactions than the di-methyl derivative, but the u.v. spectra are, in fact, almost superimposable, (Fig. 9), just as in the simpler case of the diphenylacetylenes. At the present moment the explanation is not clear, but it must be borne in mind that in u.v. absorption spectra, one is dealing with molecules in excited states, and that extrapolations from models are, at best, risky.

In the trans-stilbenes however, the only apparent change in the u.v. spectrum from that of trans-stilbene(129) itself, on the introduction of one ortho-methyl substituent, in the case of 2-methyl-trans-stilbene(128), (Section II), and two ortho-methyls,

i.e., 2,2'-dimethyl-trans-stilbene(135), (Section II), is loss of what is termed the "fine structure" of trans-stilbene(129), (Fig. 10). Haarhoven, Nivard and Havinga[149] have shown that only when all four ortho positions are substituted does the congestion become great enough to produce a marked change in the u.v. spectrum; thus, 4,4'-dimethoxy-trans-stilbene has λmax 306mμ(log ε, 4.48), 4,4'-dimethoxy-2,2'-dimethyl-trans-stilbene has λmax 300mμ(log ε, 4.39) and 4,4'-dimethoxy-2,2,2',2'-tetramethyl-trans-stilbene has λmax 273mμ (log ε, 4.24).

It is perhaps interesting to note, that in both the cis- and trans-stilbene series, once again, as is the case with the diphenylacetylenes, conversion of the methyl group into a hydroxymethyl substituent produces very little difference in the u.v. spectrum; thus, both 2-hydroxymethyl-2'-methyl-cis-stilbene(211) and 2,2'-dihydroxymethyl-cis-stilbene(214), prepared in the usual way by hydrogenation of the two acetylenic alcohols (201) and (145), respectively, using the Lindlar catalyst[41], had u.v. absorption spectra which were virtually identical to that of the parent 2,2'-dimethyl-cis-stilbene (134), (Fig. 9).

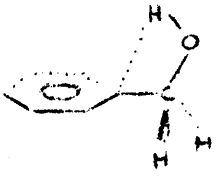
The normal conversion of the two cis- alcohols, (211) and (214), to the corresponding trans-isomers, 2-hydroxymethyl-2'-methyl-trans-stilbene(212) and 2,2'-dihydroxymethyl-trans-stilbene(215), respectively, by refluxing in a carbon tetrachloride solution containing a trace of iodine[113,114], was carried out, and the u.v. absorption

curves of (212) and (215) were very similar to that of the parent 2,2'-dimethyl-trans-stilbene(135) (Fig. 10).

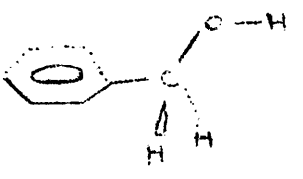
The preparations of these cis- and trans-stilbene mono-ols and diols were quite unexceptional, and went smoothly to the desired products, unlike the preparations of the fully reduced compounds, 2-hydroxymethyl-2'-methyldibenzyl(210) and 2,2'-dihydroxymethyldibenzyl(213). These were prepared for the hydrogen bonding i.r. study (see below), by hydrogenation of the acetylenic alcohols (201) and (145), respectively, using 5% palladium on charcoal as catalyst. If the hydrogenation was allowed to continue after the rapid uptake of two moles of hydrogen, slow hydrogenolysis of the labile benzylic hydroxyl groups took place, yielding the hydrocarbon, 2,2'-dimethyldibenzyl(164), identified by its m.p. and mass spectrum, and by g.l.c. comparison with an authentic sample.

(c) Intra-molecular hydrogen bonding in a series of benzyl alcohols. An infrared study.

The molecule of benzyl alcohol has a number of conformational possibilities open to it, e.g., (I) and (II).



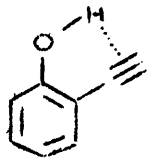
(I)



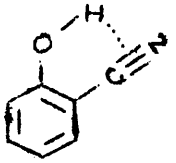
(II)

Prior to 1958, the rather low frequency of the hydroxyl stretching

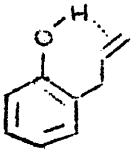
absorption,(νOH), of benzyl alcohol(216), (~3620cm.$^{-1}$), had been noted, and, in fact, some workers[150] had observed the asymmetry of this peak, but had not commented as to its origin. In 1958, Schleyer, Trifan and Bacskai[151], reported that the unsymmetrical band could be interpreted as due to the overlapping of two bands, one at ~3632cm.$^{-1}$, and a more intense one at 3615cm.$^{-1}$, corresponding to free hydroxyl (possibly conformer II), and an OH....π intramolecularly bonded hydroxyl (e.g., conformer I), respectively. The characteristic feature of a hydrogen bonded hydroxyl, is that the νOH absorption is shifted to lower frequency, and is usually broadened and intensified relative to that for the free hydroxyl. In benzyl alcohol, the bonding shift of 17cm.$^{-1}$ is small, and it might be argued that the two bands are purely due to the different orientations of the bonds with respect to one another, and that there is no"true" hydrogen bond. (Compare the νOH absorption for certain saturated alcohols[152,153]). However, OH....π hydrogen bonding, both inter- and intra-molecular, is now well authenticated[154,155], and quite large shifts have been found for some molecules, e.g., (III)[156], (IV)[157], (V)[158], (VI)[159] and (VII)[160].



(III)

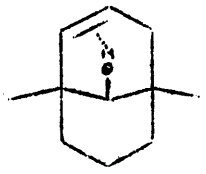


(IV)

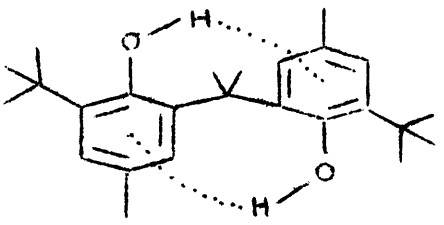


(V)

"free" OH	3623cm.$^{-1}$	3597cm.$^{-1}$	3614cm.$^{-1}$
bonded OH	3509cm.$^{-1}$	3559cm.$^{-1}$	3549cm.$^{-1}$



(VI)

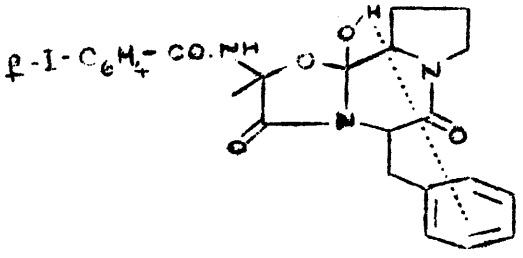


(VII)

"free" OH	3640cm.$^{-1}$	
bonded OH	3584cm.$^{-1}$	
		3484cm.$^{-1}$

Compound (VII), in fact, behaves on t.l.c. and g.l.c. like a non-polar hydrocarbon of an equivalent molecular weight.

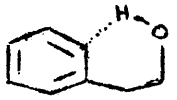
X-ray crystallographic data is now available for at least one OH....π intra-molecularly hydrogen bonded system, (VIII)[161], in the solid state.



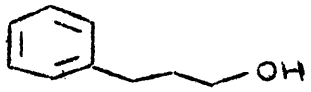
(VIII)

Schleyer, Trifan and Bacskai[151], at the same time as they reported their interpretation of the asymmetric peak of benzyl alcohol (~3620cm.$^{-1}$), reported that in β-phenylethanol (IX), OH....π intra-molecular hydrogen bonding resulted in a more substantial shift ($\Delta\nu$28cm.$^{-1}$) than that for benzyl alcohol ($\Delta\nu$, 17cm.$^{-1}$), but

at the same time the concentration of the bonded species was greatly decreased. Also, they noted that in γ-phenylpropanol (X), the bonded form had completely disappeared.



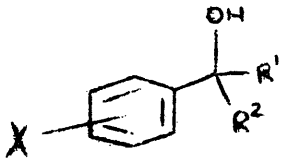
(IX)



(X)

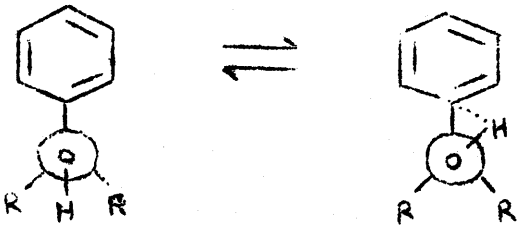
Increasing the length of the carbon chain permits a more favourable orientation for hydrogen bonding, but the greatly increased number of conformations possible means that a smaller proportion of conformers can bond with the aromatic ring; i.e., an entropy effect.

Later, Schleyer and his co-workers[162,163] examined a wide variety of substituted benzyl alcohols, and secondary and tertiary α-aromatic alcohols (XI).



(XI)

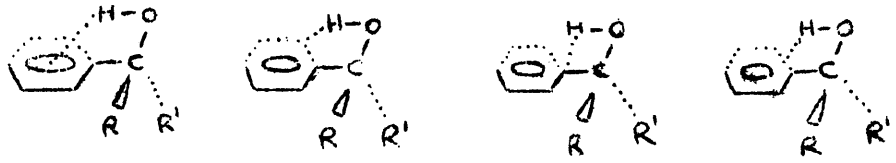
α-Aromatic alcohols were shown to exist largely or entirely in the ring-bonded form in dilute carbon tetrachloride solution. Ring substitution had little effect on $\Delta\nu$, but affected significantly the position of the free : bonded equilibrium, (XII : XIII, respectively).



(XII) (XIII)

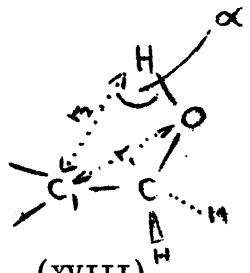
It was found that "electron-withdrawing" groups, (e.g., nitro), reduced the proportion of bonded conformer in the equilibrium, whereas "electron-repelling" groups, (methoxy, etc.), in general increased the proportion of bonded conformer. This demonstrates that a hydrogen bond between the hydroxyl and the π-electrons is being formed, since the proportion of bonded conformer can be increased or decreased by making the π-electrons more or less available, respectively, to the proton for hydrogen bonding.

At about the same time, Ōki and Iwamura[164], working on a series of meta- and para-substituted tertiary α-aromatic alcohols, obtained results similar to those of Schleyer and his co-workers[162,163], but they were able to carry the argument further. They postulated that there were four possible bonding sites for the hydrogen atom; the centre of the π-electron cloud (XIV), carbon atom C_2 (XV), carbon atom C_1 (XVI), or between carbons C_1 and C_2 (XVII).



(XIV) (XV) (XVI) (XVII)

By studying the effects on the free : bonded equilibrium produced by various meta- and para-substituents, (ortho-substitution is ruled out because of preferential hydrogen bonding to the ortho-group), they reached the conclusion that conformer (XVI), with the hydrogen bonding to carbon atom C_1, correctly represents the OH....π intra-molecularly hydrogen bonded complex.

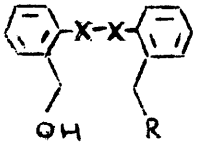


(XVIII)

This hydrogen bond is very unusual[154] in that the angle "α" enclosed by the O-H link and the hydrogen bond to C_1 (XVIII) is ~85°, and the O-C_1 distance (r_1) is ~2.5Å, the H-C_1 distance (r_2) also being ~2.5Å.

The availability of a range of systematically related benzyl alcohols (201, 210, 211 and 212) and bis-benzyl alcohols (145,213, 214 and 215) - all derived from the monobromide (159) and dibromide

(160) as described above - presented an attractive area for research. The mono-ols and diols contain the benzyl alcohol system, (XIX), ortho-substituted with a $-CH_2CH_2-$, a cis- or trans- -CH=CH-, or a -C≡C-, so that there is the opportunity for interaction with these groups, in addition to, or perhaps in competition with, bonding to the parent benzene ring.



where -X-X- is $-CH_2CH_2-$, -CH=CH- (cis or trans), or -C≡C-.
R is H or OH.

(XIX)

Furthermore, there is the possibility of interaction with the other benzene ring or benzyl alcohol grouping in some cases. Quite complex bands due to the hydroxyl stretching absorptions were therefore to be expected. Successful interpretation of these bands, might afford an appreciation of the energetic and steric requirements of the benzylic hydroxyl for intra-molecular hydrogen bonding.

The authenticity of the alcohols is established by mode of preparation, by the i.r. and u.v. spectra, and, in most cases, by mass spectrometry. The purity is established by the sharp melting point behaviour and by t.l.c. (silica, and silica impregnated with silver nitrate); n.m.r. studies, which would have been desirable, were precluded by the relative insolubility of the compounds in the common solvents.

The u.v. spectra have been discussed above, and appear to be of little direct assistance in the interpretation of the i.r. spectral data, although some steric effects are evident.

In some cases the hydroxyl absorptions might conceivably be interpreted in terms of mixtures of related compounds, [e.g., the trans- diol (215) and the cis- diol(214)], but the definition afforded by t.l.c. on silica impregnated with silver nitrate was sufficient to exclude this possibility. One is therefore in a position to interpret the observed bands purely in terms of the conformational equilibrium exhibited by the individual mono-ol or diol.

For such a study, the first essential is to ensure that the substance examined is present only as a monomer, and that inter-molecularly associated species are absent. This is achieved by making the νOH measurements in very dilute solution in carbon tetrachloride, a solvent which is fairly transparent in this region of the i.r., even at long path lengths. Inter-molecular association is, in fact, seen in some of the more concentrated solutions examined. The νOH band for OH....OH inter-molecular hydrogen bonding diminishes in intensity in going from high to low concentrations, whereas the intra- : "free" ratio is constant. In the mono-ol (201), the inter-molecularly bonded hydroxyl absorbs at ~3495cm.$^{-1}$, (Table 5 and Fig. 11), and is on the point of disappearing at a concentration of about 0.003 molar. However, in some cases (see Table 7), the association persisted to very low concentrations, and recourse had

to be made to 9 cm. cells and very dilute solutions, before such bands could be almost entirely eliminated. Very persistent inter-molecular association (down to ~0.0005 molar) is known in certain types of dihydroxy compounds[165,166].

Two compounds (145 and 201) were examined in a second solvent, chloroform. Chloroform is a relatively polar solvent compared with carbon tetrachloride, and undoubtedly associates with basic centres in the solute by hydrogen bonding, e.g., $Cl_3C-H....B$. Consequently, it has the effect of slightly lowering and broadening the "free" hydroxyl stretching frequency of dissolved alcohols, and of reducing the extent of self-association of alcohols at a given concentration, compared with carbon tetrachloride[167]. The two compounds do show this behaviour, but the resultant broadening of the νOH absorption bands has obliterated the detail revealed in the carbon tetrachloride spectra, (Table 6 and Fig. 12). Also noteworthy is the shift to lower frequency of the intra-molecular band ($\Delta\nu, \sim 40 cm.^{-1}$) in the case of (145), and the inter-molecular band ($\Delta\nu, \sim 35 cm.^{-1}$) in the case of (201). Also, it should be pointed out that chloroform, by virtue of its hydrogen bonding capacity, can affect equilibria involving monomeric species, and thereby change the intra : "free" ratios[167].

The observed νOH absorption band data is assembled in Tables 5-8, and illustrated in Figs. 11-14. A number of points are immediately obvious.

(i) The spectra are expectedly complicated, i.e., each compound shows at least three bands,[except benzyl alcohol(216)], even at such high dilution that inter-molecular hydrogen bonding is, to all intents and purposes, eliminated.

(ii) In every case, [except o-iodobenzyl alcohol(172)], the most prominent band is at about 3615cm.$^{-1}$, roughly corresponding to the most prominent band in benzyl alcohol.

(iii) In spite of the complexity of the shape of the absorption bands, it is clear that each spectrum is composed of several independent bands, which, because of their breadth or close separation, have merged, and are seen as shoulders on asymmetric bands. Nevertheless, it is possible to assign the approximate frequency (ν), band width ($\Delta\nu_{\frac{1}{2}}$) and intensity (ε) to these absorptions, by "graphical band construction".

(iv) There is some considerable variation in the degree of self-association over the concentration ranges examined, which must reflect differences in stereochemistry, and thereby in the availability or otherwise, of the hydroxyls for inter-molecular hydrogen bonding.

Inter-molecular Association. As already mentioned, the initial experiments in any hydrogen bonding study must be those designed to distinguish between inter- and intra-molecular hydrogen bonding. All the compounds under study have been examined at various concentrations in carbon tetrachloride solution. The bands which diminish

in intensity on progressive dilution have been listed in Table 7. In some cases, the lowest concentrationd which could be handled experimentally still showed a band of reduced intensity compared with the previous higher concentration. In these cases it is a reasonable assumption that the band would disappear on further dilution, and is therefore to be ascribed to an inter-molecular hydrogen bond. Examples of this are provided by the diols (213, 214 and 215), (Table 7 and Fig. 13). A typical dilution study in carbon tetrachloride is shown in Fig. 11, which demonstrates the progessive disappearance of the inter-molecularly associated band at ~3495cm.$^{-1}$. In this case, the associated band is still detectable at a concentration of 0.0034 molar, but has completely disappeared at 0.00088 molar.

The data in Table 7 indicates that one can distinguish some compounds which display abnormally persistent association. As might be expected, (see above), the diols associate more strongly than the mono-ols. However, certain diols associate particularly strongly, e.g., (213, 214 and 215), and these compounds presumably have hydroxyls which are suitably orientated for some form of cyclic complexes involving dimeric, trimeric and tetrameric species, (c.f. the novalaks[160]). Further studies are required to elucidate the factors which bring about abnormally persistent association of this type.

Intra-molecular Hydrogen Bonding. With the exception of those compounds displaying abnormally persistent inter-molecular association, the mono-ols and diols exhibit spectra (Fig. 13) in dilute solution in carbon tetrachloride, which are interpretable solely in terms of the various conformations adopted by the individual molecule in the solvent cage.

As already discussed, several groups of workers have examined, in some detail, the spectra of benzyl alcohol and related compounds[162-164]. The unsymmetrical band of benzyl alcohol(216), illustrated in Fig. 13, has been dissected into two overlapping bands, at 3640cm.$^{-1}$ and 3618cm.$^{-1}$. The graphical separation is illustrated in Fig. 14. Such treatment is helpful in treating bands of complex shape, but is necessarily somewhat subjective, and ideally requires curve analysis with an electronic computor[168]. However, graphical treatment of three of the substituted benzyl alcohols studied, is shown in Fig. 14. A comparison of the results given by this method, against the results obtained in the more conventional way, is given in Table 8. It should be stressed that the results obtained, while demonstrating the principle involved, are not sufficiently reproducible due to difficulties in constructing the curves, and therefore it was not considered advisable to use these results in the interpretation of the observed spectra.

The premise on which such band analysis is based is, of course,

that a group X-H, which is vibrating in a symmetrical environment, will give rise to a symmetrical (Lorentz) absorption band[169]. A symmetrical band will also arise where the band is the summation of a number of closely spaced sharper bands, corresponding to a number of conformers of similar energy content, among which the molecular population is fairly evenly distributed. The unsymmetrical bands arise when one or more of the conformations involves a sufficiently different force constant for the X-H link.

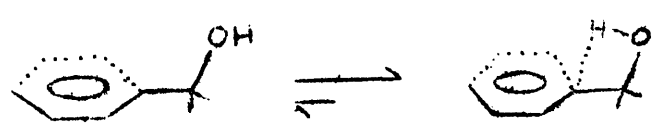
The assignments of the individual absorption bands of the compounds examined now follow.

(i) Benzyl alcohol(216).

The literature studies[162-164] provide the following assignments:-

3635cm.$^{-1}$	3618cm.$^{-1}$
νOH "free"	νOH bonded to C_1 of aromatic ring.
33%	67%

The percentages give the approximate proportions of the different conformers in the equilibrium mixture, and are only intended to be taken as a rough guide. Thus the equilibrium may be represented as follows:-



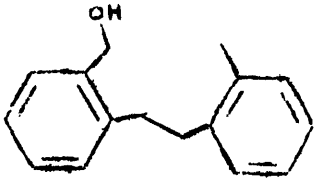
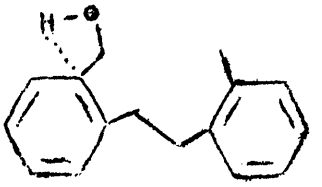
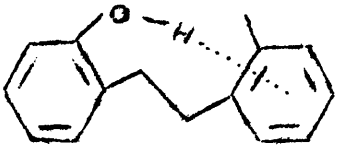
3635cm.$^{-1}$ 3618cm.$^{-1}$

(ii) o-Iodobenzyl alcohol(172).

There appears to be three overlapping bands at 3640cm.$^{-1}$, 3620cm.$^{-1}$ and ~3592cm.$^{-1}$. It seems reasonable to assign those corresponding in frequency to the two bands of benzyl alcohol, i.e., 3640cm.$^{-1}$ and 3620cm.$^{-1}$, to the "free" hydroxyl and hydroxyl bonded to C_1 of the aromatic ring, respectively, but here the free conformer is dominant. The shoulder at ~3592cm.$^{-1}$ is presumably to be assigned to OH....Iodine intra-bonding. It would be interesting to examine the bromide and chloride for a similar absorption. Tichy[170] has summarised the available data relating to intra-molecular hydrogen bonding between the hydroxyl group and various basic centres. The results are reproduced in Table 9, and show the wide variety of centres which are capable of donating electrons to a proton for hydrogen bonding.

(iii) 2-Hydroxymethyl-2'-methyldibenzyl(210).

Benzyl alcohol provides valuable comparison data for this alcohol; thus the only additional basic site, available to the proton for hydrogen bonding, is the second benzene ring, which is attatched to the first by a saturated two carbon chain. Hence we can confidently propose the following mixture of conformers, with their respective assigned frequencies and approximate relative proportions:-

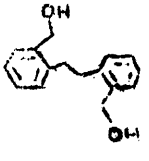
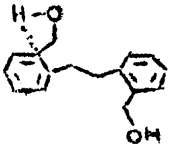
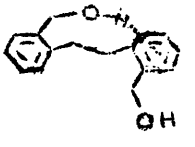
νOH 3648cm.$^{-1}$ 3611cm.$^{-1}$ 3533cm.$^{-1}$

5% 80% 15%

(All three conformers are presumed to be interconvertible).

(iv) 2,2'-Dihydroxymethyldibenzyl(213).

In this case, the only additional feature to (210) is the second hydroxyl group substituted on the methyl on the second benzene ring. The only additional band is that at 3575cm.$^{-1}$ and this is presumably due to OH....OH intra-molecular hydrogen bonding. It is rather surprising that the absorption is at such high frequency in view of the close approach which is possible between the two groupings. However, the low intensity of the band is understandable in terms of the high degree of conformational freedom open to the molecule (c.f. hexane-1,6-diol, which does not display any intra-molecular bonding[171]).


νOH ~3640cm.$^{-1}$ 3618cm.$^{-1}$ 3535cm.$^{-1}$ 3575cm.$^{-1}$

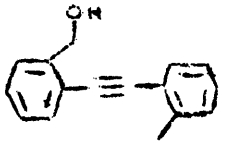
15% 60% 10% 15%

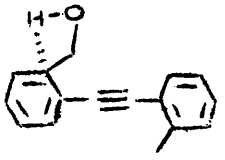
The above representation of the conformers present is not complete, since there are several more possibilities, e.g., both hydroxyl

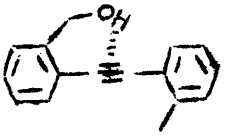
groups could be bonding to their respective "parent" rings at the same time, etc.

(v) 2-Hydroxymethyl-2'-methyldiphenylacetylene(201).

For this alcohol, the saturated mono-ol (210) was used for comparison, and it is clear that OH....π (second aromatic ring) bonding has been eliminated. This was expected, since the other aromatic ring is held rigidly at too great a distance for intra-molecular bonding with the hydroxylic proton. (O....C distance is ~4Å from Dreiding models). The shoulder at ~3595cm.$^{-1}$ is assigned as OH....π (carbon-carbon triple bond). The following three conformers are therefore presumed to be present in the equilibrium mixture:-





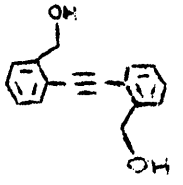


νOH	3637cm.$^{-1}$	3618cm.$^{-1}$	~3595cm.$^{-1}$
	35%	40%	25%

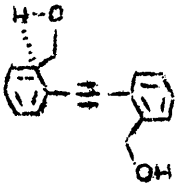
(vi) 2,2'-Dihydroxymethyldiphenylacetylene(145).

This diol (145), which corresponds to the previously described mono-ol (201), has an additional basic site for bonding to the hydroxyl, and the consequent OH....OH intra-molecular hydrogen bond accounts for the prominent band at 3507cm.$^{-1}$. The OH....π (carbon-carbon triple bond) is however still present as a small peak at ~3580cm.$^{-1}$. (Figs. 13 and 14). The approximate proportion

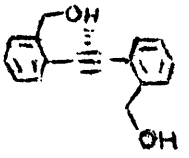
of the four (at least) conformers is given below.



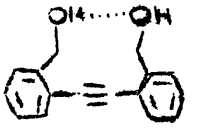
νOH 3637cm.$^{-1}$
25%



3617cm.$^{-1}$
45%



~3580cm.$^{-1}$
10%



3507cm.$^{-1}$
20%

This diol is a particularly interesting compound, as the two benzene rings are linked by the rigid triple bond, and the benzene rings bearing the hydroxymethyl groups, although free to rotate round the axis of the triple-bond, have much less conformational freedom than those in (213). Of course, the -CH_2OH groups are normally free to rotate with respect to the benzene rings to which they are attatched, but when both are at almost closest approach, the O....O distance is ~2.5Å, and the situation appears (from models) to be ideally suited to bonding.

(vii) Substituted stilbene mono-ols and diols (211, 212, 214 and 215).

The carbon-carbon double bond link between the two aromatic rings introduces several new features. The rigid and cylindrically symmetrical acetylene unit of (145) aand (201) is replaced by the cis- or trans- double bond. This brings about (a) complications arising from hydrogen-hydrogen interactions - steric restriction of coplanarity of the benzene ring and the double bond (c.f. u.v. evidence above for profound steric disturbances), (b) the π-electrons

(double bond) required for hydrogen bonding being available only in certain directions, (c) additional conformational freedom which means that several different conformations of the interacting groups are possible, e.g., in the cis- mono-ol (211), the hydroxyl group could be orientated so as to produce "free" hydroxyl, bonded OH....π (parent aromatic ring), bonded OH....π (double bond) at various angles,and OH....π(other aromatic ring), again at various angles. In the event, the observed bands are interpreted in the following way:-

(211)

νOH	~3635cm.$^{-1}$	3618cm.$^{-1}$	3580cm.$^{-1}$	~3535cm.$^{-1}$
	OH "free"	OH....π (parent aromatic ring)	OH....π (double bond)	OH....π (second aromatic ring)
	25%	55%	15%	5%

(214)

νOH	~3638cm.$^{-1}$	3619cm.$^{-1}$	3585cm.$^{-1}$	~3535cm.$^{-1}$
	OH "free"	OH....π (parent aromatic ring)	OH.... π (double bond)	OH....π (second aromatic ring)
	25%	50%	15%	10%

It would appear that OH....OH intra-molecular bonding is surprisingly absent in this diol, compared to the acetylenic diol (145).

(212)

νOH	~3640cm.$^{-1}$	3618cm.$^{-1}$	~3580cm.$^{-1}$	~3535cm.$^{-1}$
	OH "free"	OH....π (parent aromatic ring)	OH....π (double bond)	OH....π (second aromatic ring)
	20%	60%	5%	15%

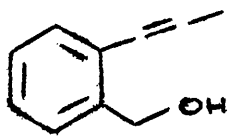
The absorption band at ~3535cm.$^{-1}$ was not expected on the basis of models, since the second ring appears to be just too far away for bonding. Another possible interpretation of this band, is that there could be two possible sites on the double bond to which the proton bonds, e.g., to each carbon atom of the double bond.

(215)

νOH	~3640cm.$^{-1}$	3618cm.$^{-1}$	3584cm.$^{-1}$	~3535cm.$^{-1}$
	OH "free"	OH....π (parent aromatic ring)	OH....π (double bond)	OH....π (second aromatic ring)
	20%	50%	20%	10%

Again, there is no apparent OH....OH intra-molecular bond in this diol, and the OH....π (second aromatic ring) is also again unexpectedly present.

However, it should be pointed out that these assignments can only be tentative because of (a) lack of adequate reference compounds, e.g.,(XX),



(XX)

as cis- and trans- double bond isomers, and (b) the complexity of the conformational situation, as indicated.

In conclusion, the results of the study may be summarised. The spectral observations reveal that flexible molecules of this type bearing a number of basic sites, adopt a number of conformations which can be detected by the characteristic frequencies of the intra-molecular hydrogen bonds. The relative proportions of these conformations are very sensitive to the functional groups present, partly as a result of the variation in the electron density available for hydrogen bonding, and partly as a consequence of the changes in the flexibility of the molecules. Further studies with carefully chosen molecules, and computer analysis of the absorption bands, should permit a much more quantitative and precise evaluation of this interesting area of research. It is evident that such a study should lead to a better appreciation of the steric, electronic and entropy effects controlling the conformational equilibrium of flexible molecules in solution - an area of chemistry about which relatively little is known.

EXPERIMENTAL. SECTION III.

Treatment of 2,2'-dibromomethyldiphenylacetylene(160) with zinc in acetamide.

The dibromide (160) (100mg.) in solution in molten acetamide (5gm.) was stirred and heated (150°) in the presence of zinc dust (250mg.) for 4 hr. The reaction mixture was cooled and water added. The aqueous suspension was extracted thoroughly with ether, the combined ethereal extracts washed with water, and dried (magnesium sulphate). Filtration and evaporation of the ether gave a yellow oil (56mg.), which was shown by t.l.c. (silica - petrol as eluent) to contain two compounds, the slower-running spot being identical with the starting dibromide (160), the faster-running spot having the same R_F as 2,2'-dimethyldiphenylacetylene(158). Preparative t.l.c. (silica, 1mm. thick - eluted three times with petrol) gave the pure dibromide (160) (7mg. - 7% recovery), identical with the starting material, by t.l.c., i.r. and u.v., and the dimethyl derivative (158), (33mg. - 58%), by comparison with an authentic sample, t.l.c., i.r. and u.v. Hydrogenation of the 2,2'-dimethyldiphenylacetylene(158) (5% Pd-C in ethyl acetate) gave 2,2'-dimethyldibenzyl(164), identical with an authentic sample by g.l.c. (1% S.E.30 on "Gas Chrom P", 100-120 mesh, at 125°, retention time 7 min.). No 1,2:5,6-dibenzocycloocta-1,5-diene-3-yne(185) appears to have been present prior to hydrogenation, since the gas chromatograms of the hydrogenated product showed no peak corresponding to

the reduced 1,2:5,6-dibenzocycloocta-1,5-diene(163).

Treatment of 2,2'-dibromomethyldiphenylacetylene(160) with ammonium sulphide.

A solution of the dibromide(160) (100mg.) in chloroform (5ml.) was stirred at room temperature for 48 hr. with a mixture (10ml.) of equal volumes of ammonium hydroxide solution (0.88), and ammonium hydroxide solution (0.88) which had been saturated with hydrogen sulphide. The chloroform layer was separated, and the aqueous layer extracted twice with chloroform. The combined chloroform extracts were washed with water and dried (magnesium sulphate). Filtration and evaporation gave a crude pale yellow solid (86mg.), m.p. 155-165° fast. T.l.c. (silica - 20% ethyl acetate-petrol as eluent) gave two spots, one on the origin, the other with R_F 0.7. The starting dibromide (160) under these conditions had R_F 0.6. Both the i.r. and u.v. spectra of this crude solid were uninformative. A sodium fusion elements test was negative for halogen and nitrogen, positive for sulphur. On attempted sublimation, the solid decomposed at ~130°. Attempted purification by preparative t.l.c. resulted in several new bands appearing, probably due to oxidation on the plate. Crystallisation from organic solvents was unsuccessful, due to the lack of solubility of the product, which also precluded the determination of its n.m.r. spectrum. The mass spectrum of the crude solid showed no obvious molecular ion,

Attempted preparation of 3,4:7,8-dibenzo-1-oxacyclonona-3,7-diene-5-yne(186).

(a) A solution of the diol (145) (24mg.) and p-toluenesulphonyl chloride (22mg. - 1.15 equivalents) in dry pyridine (1ml.) was allowed to stand at room temperature for 72 hr., then poured into water and quickly extracted four times with ether. The combined ethereal extracts were washed with a little water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave the unchanged diol (145) (21mg. - 88% recovery), t.l.c., i.r. and u.v. unchanged.

(b) A solution of the diol (145) (40mg.) and p-toluenesulphonyl chloride (36mg. - 1.15 equivalents) in dry pyridine (2ml.) was allowed to stand at room temperature for 72 hr., and then the pyridine was removed under reduced pressure to give a solid (113mg.), whose i.r. spectrum, although complex, was devoid of some of the bands due to p-toluenesulphonyl chloride itself. T.l.c., however, showed only the starting alcohol (145), probably due to hydrolysis taking place on the chromatoplate. The crude solid was added to excess of the dimsyl carbanion in dimethylsulphoxide, prepared in the usual way[143], i.e., by dissolving sodium hydride in dry dimethylsulphoxide at ~70° under nitrogen, and the reaction mixture allowed to stand at room temperature for 48 hr. Water was then added, and the reaction mixture thoroughly extracted with ether, the combined ethereal extracts washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent and purification of the product by

preparative t.l.c., gave the starting diol (145) (30mg. - 75% recovery), identical with an authentic sample by i.r., u.v. and t.l.c. No compound corresponding to the cyclic ether (186) or either of the enol-ethers (199 or 200) was isolated.

Conversion of the diol (145) to the diacetate (198).

The diol (145) (10mg.) in dry pyridine (1ml.) containing two drops of acetic anhydride, was heated under reflux for 1 hr. The reaction mixture was cooled, poured into water and extracted with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the ether gave the diacetate (198) (13mg. - 95%), identical by i.r., u.v. and t.l.c. with an authentic sample.

Reaction of 2-hydroxymethyl-2'-methyldiphenylacetylene(201) with dimsyl sodium.

The mono-ol (201) (45mg.) was added to the carbanion of dimethylsulphoxide[143], prepared by dissolving sodium hydride (48mg.) in dry dimethylsulphoxide (1ml.) at 70° under nitrogen. The reaction mixture was allowed to stand at room temperature for 48 hr. It was then poured into water and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a crude semi-solid (51mg.), whose i.r. spectrum (film) was

devoid of absorption in the region of 3600cm.$^{-1}$, (νOH), and showed absorption at ~835cm.$^{-1}$, which is characteristic of a tri-substituted double bond. This is in agreement with either of the expected enol-ether structures, (203 or 204). The u.v. spectrum (ethanol) of the crude product was dominated by the characteristic absorption of the starting alcohol (201), which could also be seen to be present in a small amount by t.l.c., although not by i.r. However, on attempted purification of the product by preparative t.l.c. (silica, 1mm. thick - petrol as eluent), the spot which had previously been assigned to the enol-ether, was found to be present in only a very small amount (~2%), and the bulk of the material from the plate was found near the origin, (33mg.). This oil now showed the presence of a hydroxyl group in its i.r. spectrum (liquid film), νOH ~3500cm.$^{-1}$, and a carbonyl function, νC=O ~1700cm.$^{-1}$. This oil is thought to contain one or other or both of the keto-alcohols (205 or 206), formed by hydrolysis of the reactive enol-ether on the chromatoplate.

Preparation of 2,2'-diacetoxymethyldiphenylacetylene(198).

A solution of 2,2'-dibromomethyldiphenylacetylene(160) (100mg.) and fused sodium acetate(225mg.) in acetic acid (3ml.) was heated under reflux for 4 hr., cooled, and poured into water. The resulting white precipitate was extracted three times with ether, and the combined ethereal extracts washed successively with water, saturated aqueous sodium carbonate solution and water, dried (magnesium

sulphate) and filtered. Evaporation of the solvent gave the diacetate (198), (90mg. - 99%) as needles, m.p. 83.5-84.5° on sublimation at 240°/0.1mm. Mass spectrum: molecular ion at 322, ($C_{20}H_{18}O_4$ requires M.W. 322). T.l.c. (silica - 10% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.15. The i.r. spectrum (nujol mull) showed typical acetate carbonyl absorption at ~1740cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 271mμ, 277mμ, 285mμ, 294mμ and 304mμ, (log ε, 4.05, 4.09, 4.19, 4.07 and 4.12, respectively), (Fig. 6).

Preparation of 2-acetoxymethyl-2'-methyldiphenylacetylene(202).

The mono-acetate (202) was prepared from a solution of 2-bromomethyl-2'-methyldiphenylacetylene(159) (249mg.) and fused sodium acetate (300mg.) in acetic acid (3ml.) as in the preceding experiment. The mono-acetate (202) was obtained as a colourless oil, b.p. 220°/0.2mm. (block), (201mg. - 87%). Mass spectrum: molecular ion at 264, ($C_{18}H_{16}O_2$ requires M.W. 264). T.l.c. (silica - 10% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.4. The i.r. spectrum (liquid film) showed typical acetate carbonyl absorption at ~1740cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 271mμ, 277mμ, 285mμ, 294mμ and 304mμ, (log ε, 4.10, 4.15, 4.26, 4.12 and 4.18, respectively), (Fig. 6).

Preparation of 2,2'-dihydroxymethyldiphenylacetylene(145).

The diacetate (198) (70mg.) in dry ether (2ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (50mg.- 6 equivalents) in ether (5ml.). The reaction mixture was stirred and heated under reflux for 2 hr., cooled, and a saturated aqueous solution of ammonium sulphate was carefully added. The ether layer was separated, and the aqueous layer extracted three times with ether. The combined ethereal extracts were washed with a little water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave the diol (145), (48mg. - 93%), as needles, m.p. 127-128° from water. Mass spectrum: molecular ion at 238, ($C_{16}H_{14}O_2$ requires M.W. 238). T.l.c. (silica - 20% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.05. The i.r. spectrum (nujol mull and KCl disc) was devoid of any absorption in the region of 1700cm.$^{-1}$, but showed typical hydroxyl stretching at ~3400cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 271mμ, 277mμ, 285mμ, 294mμ and 304mμ, (log ε, 4.32, 4.36, 4.48, 4.35 and 4.40, respectively), (Fig. 6).

Preparation of 2-hydroxymethyl-2'-methyldiphenylacetylene(201).

The mono-ol (201) was prepared as in the preceding experiment, by adding a solution of the mono-acetate (202) (195mg.) in dry ether (3ml.) to a stirred suspension of lithium aluminium hydride (80mg. - 6 equivalents) in dry ether (6ml.). The mono-ol (201) was obtained (141mg. - 86%) as needles, m.p. 63-64° from petrol. Mass spectrum:

molecular ion at 222, ($C_{16}H_{14}O$ requires M.W. 222). T.l.c. (silica - 20% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.3. The i.r. spectrum (melted film and KCl disc) was devoid of absorption in the 1700cm.$^{-1}$ region, but showed typical hydroxyl stretching at ~3400cm.$^{-1}$. The u.v. spectrum (ethanol) had λmax 271mμ, 277mμ, 285mμ, 294mμ and 304mμ, (log ε, 4.16, 4.21, 4.31, 4.17 and 4.23, respectively), (Fig. 6).

Preparation of 2,2'-dihydroxymethyl-cis-stilbene(214).

The acetylenic diol (145) (10.5mg.) in ethanol, was hydrogenated using the Lindlar catalyst[41] (lead-palladium-calcium carbonate, poisoned with a trace of quinoline). The hydrogenation was stopped after the uptake of one mole of hydrogen, the solution filtered, and the catalyst washed thoroughly with ethanol. Evaporation of the solvent from the combined filtrate and washings gave the cis-diol (214) (crude 10.5mg. - 99%) as needles, m.p. 106-107° from water. T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.2. The u.v. spectrum (ethanol) was characteristic of cis-stilbenes (Fig. 9), and was devoid of any absorption due to the starting diol (145).

Preparation of 2-hydroxymethyl-2'-methyl-cis-stilbene(211).

The acetylenic alcohol (201) (11mg.) in ethanol, was hydrogenated with one mole of hydrogen over the Lindlar catalyst[41] as in the

preceding experiment. The cis-mono-ol (211) was obtained (crude 10.5mg. - 95%) as needles, m.p. 41-42° from petrol. T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.6. Again the characteristic u.v. spectrum (ethanol), (Fig. 9), was devoid of absorption due to the starting alcohol (201).

Preparation of 2,2'-dihydroxymethyl-trans-stilbene(215).

A solution of the cis-diol (214) in carbon tetrachloride containing a trace of iodine, was heated under reflux for 4 hr., cooled, washed with aqueous sodium thiosulphate solution to remove the iodine, dried (calcium chloride) and filtered. Evaporation of the solvent gave the trans-diol (215) in quantitative yield, needles, m.p. 158-159° from water. (Bergmann and Pelchowicz[172] give m.p. 162°). T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.15. The u.v. spectrum (ethanol), (Fig. 10), showed a shift of 26mμ to longer wavelength than the cis-isomer, which is characteristic of isomerisation of cis-stilbenes to trans-stilbenes. The i.r. spectrum (CS_2 solution) showed absorption at ~965cm.$^{-1}$, (νCH=CH trans).

Preparation of 2-hydroxymethyl-2'-methyl-trans-stilbene(212).

The cis-mono-ol (211) was isomerised to the trans-mono-ol (212) as in the preceding experiment, and (212) was obtained in

quantitative yield as needles, m.p. 47-48° from petrol. T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot R_F 0.55. The u.v. spectrum (ethanol), (Fig. 10), again showed a characteristic shift of 27mμ to longer wavelength than the cis-isomer. The i.r. spectrum (CS_2 solution) showed absorption at ~960cm.$^{-1}$, (νCH=CH trans).

Preparation of 2,2'-dihydroxymethyldibenzyl(213).

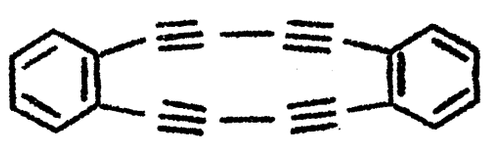
The acetylenic diol (145) (10.1mg.) in ethanol, was hydrogenated over 5% palladium on charcoal as catalyst. The hydrogenation was stopped after the uptake of two moles of hydrogen, the solution filtered, and the catalyst washed thoroughly with ethanol. Evaporation of the solvent from the combined filtrate and washings gave the saturated diol (213), (10mg. - 97%) as needles, m.p. 150-151° from water. (Bergmann and Pelchowicz[172] give m.p. 151°). Mass spectrum: molecular ion at 242, ($C_{16}H_{18}O_2$ requires M.W. 242). T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.27. The u.v. spectrum lacked any absorption due to a stilbene or diphenylacetylene derivative.

It is important to stop the hydrogenation after the uptake of the two moles of hydrogen, (which is very fast), since in one experiment where the hydrogenation was allowed to proceed for a longer time, the only compound isolated was 2,2'-dimethyldibenzyl (164), m.p. 56-57° on sublimation at 100°/0.2mm. (Cope and

Fenton[122] give m.p. 56-58°). Mass spectrum: molecular ion at 210, ($C_{16}H_{18}$ requires M.W. 210). The compound was identical with an authentic sample (Section II) by t.l.c. (silica - petrol as eluent) and g.l.c. (1% S.E.30 on "Gas Chrom P", 100-120mesh, at 125° - retention time, 7 min.).

Preparation of 2-hydroxymethyl-2'-methyldibenzyl(210).

The acetylenic alcohol (201) (9.4mg.) in ethanol, was hydrogenated with two moles of hydrogen as in the preceding experiment. The saturated mono-ol (210), (9.2mg. - 96%) was obtained as needles, m.p. 33-34° from petrol. Mass spectrum: molecular ion at 226, ($C_{16}H_{18}O$ requires M.W. 226). T.l.c. (25% silver nitrate on silica - 30% ethyl acetate-petrol as eluent) showed only one spot, R_F 0.75, but on running a vastly overloaded silica plate in petrol, traces of 2,2'-dimethyldibenzyl(164) could be seen. The u.v. spectrum again lacked the characteristic absorption of a stilbene or diphenylacetylene derivative.



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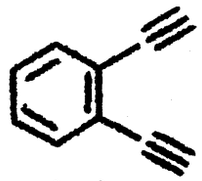

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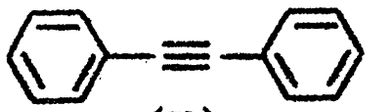

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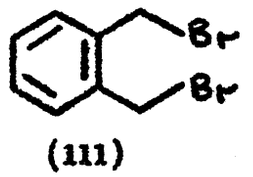

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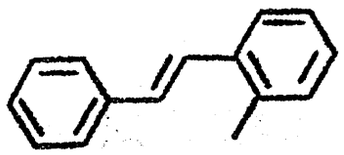

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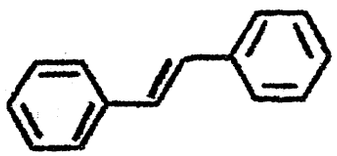

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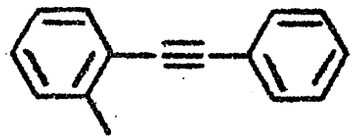

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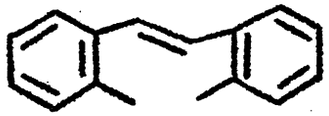

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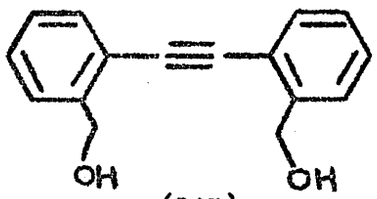

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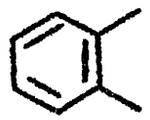

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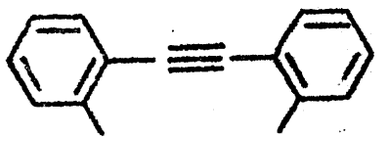

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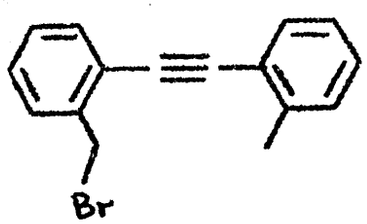

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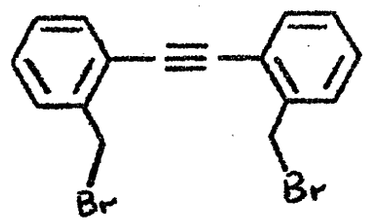

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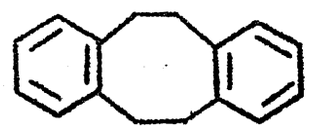

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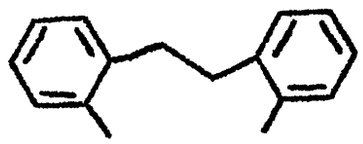

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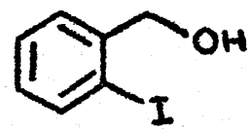

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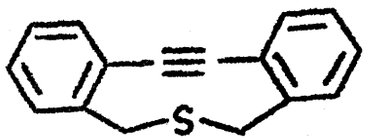

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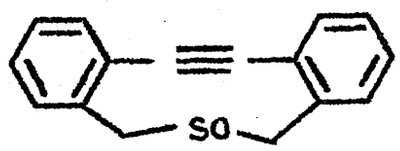

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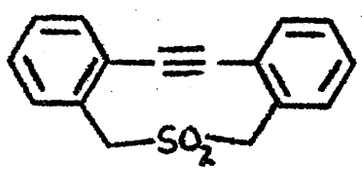

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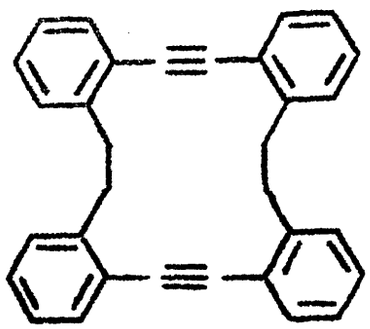

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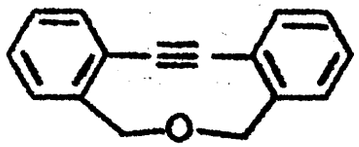

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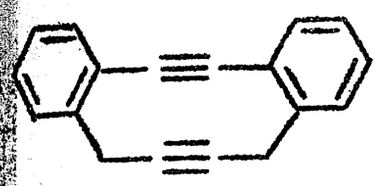

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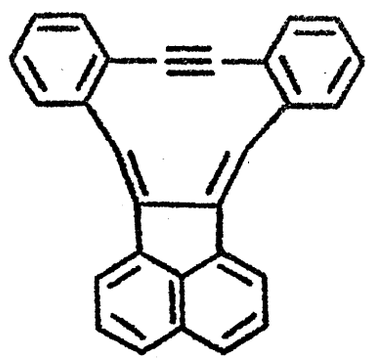

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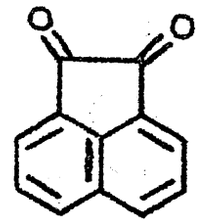

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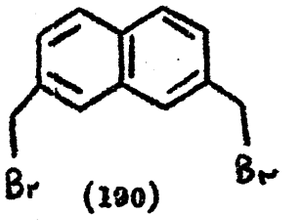

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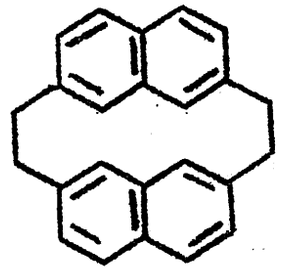

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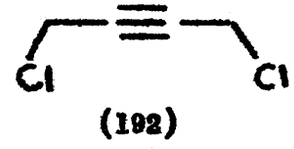

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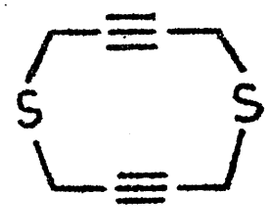

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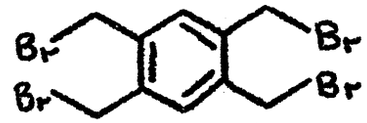

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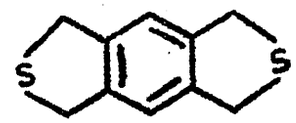

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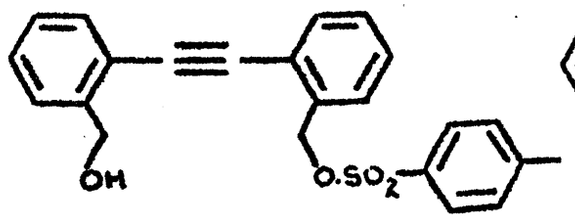

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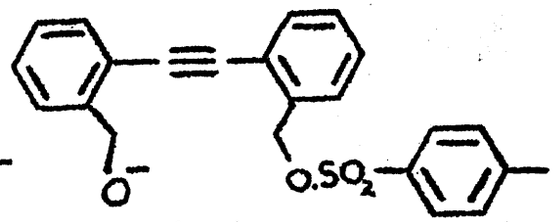

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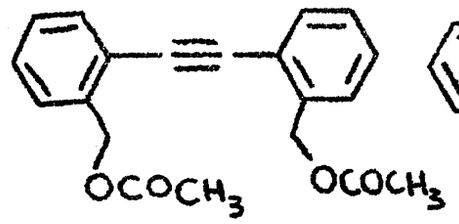

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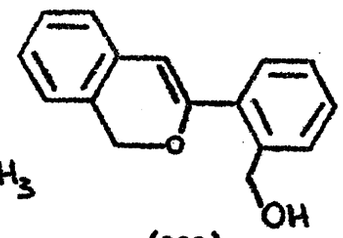

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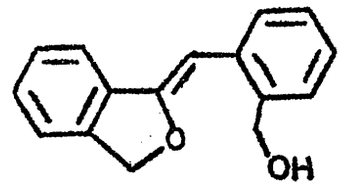

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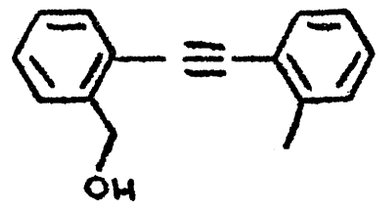

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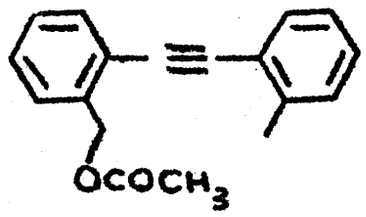

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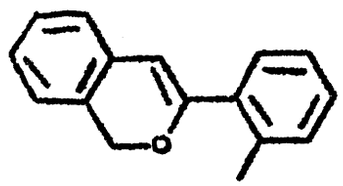

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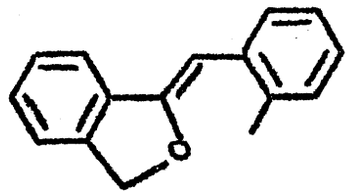

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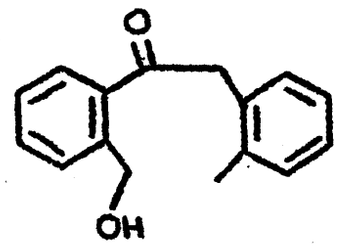

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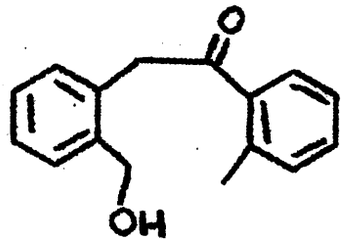

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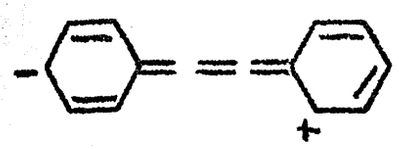

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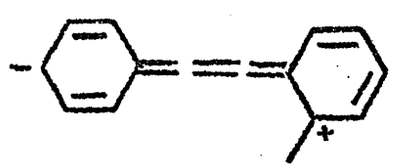

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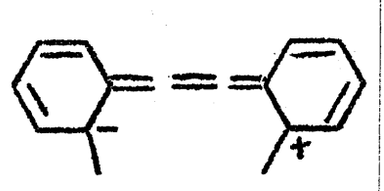

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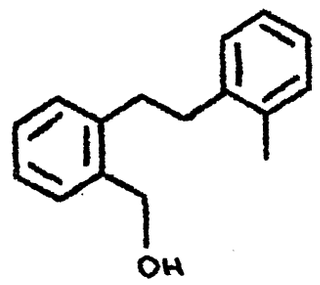

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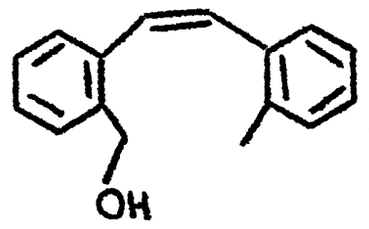

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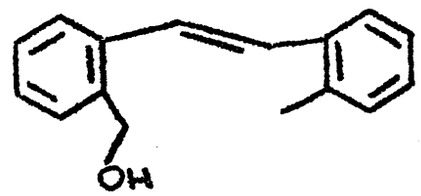

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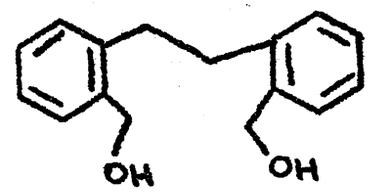

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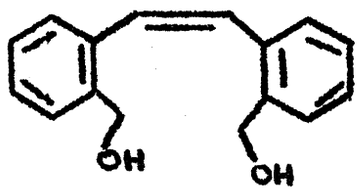

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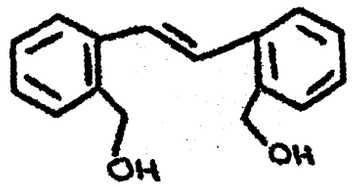

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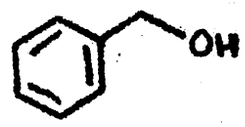

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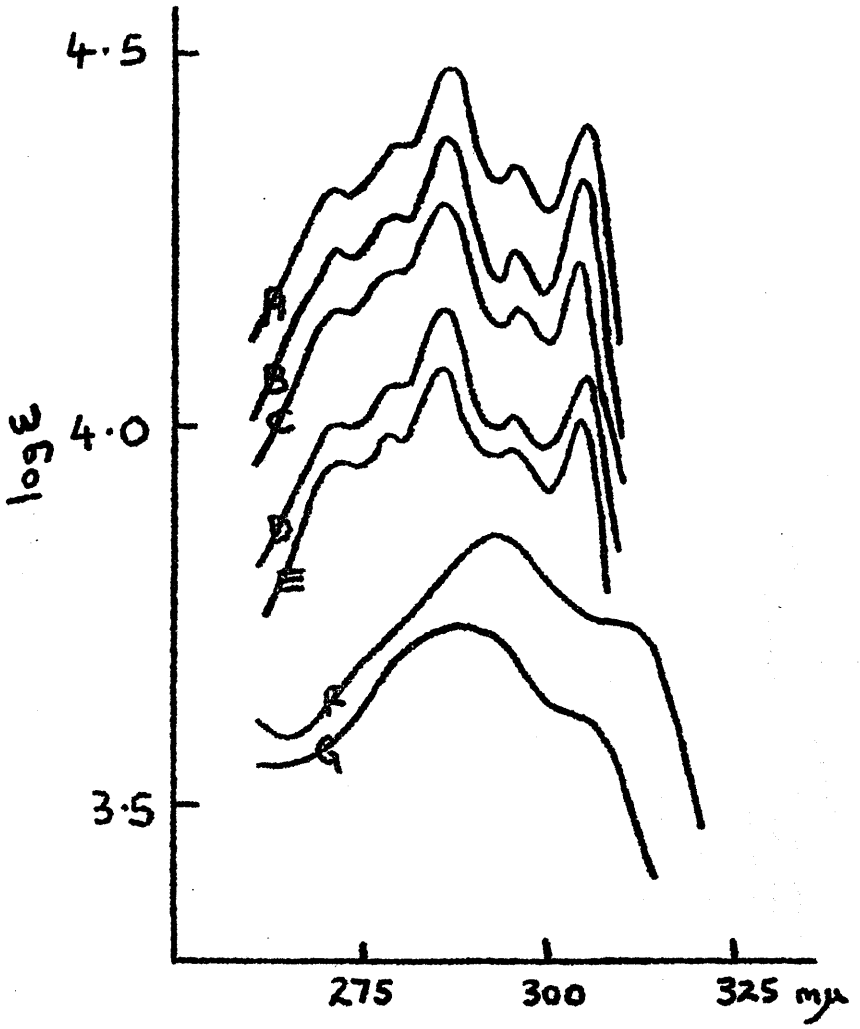
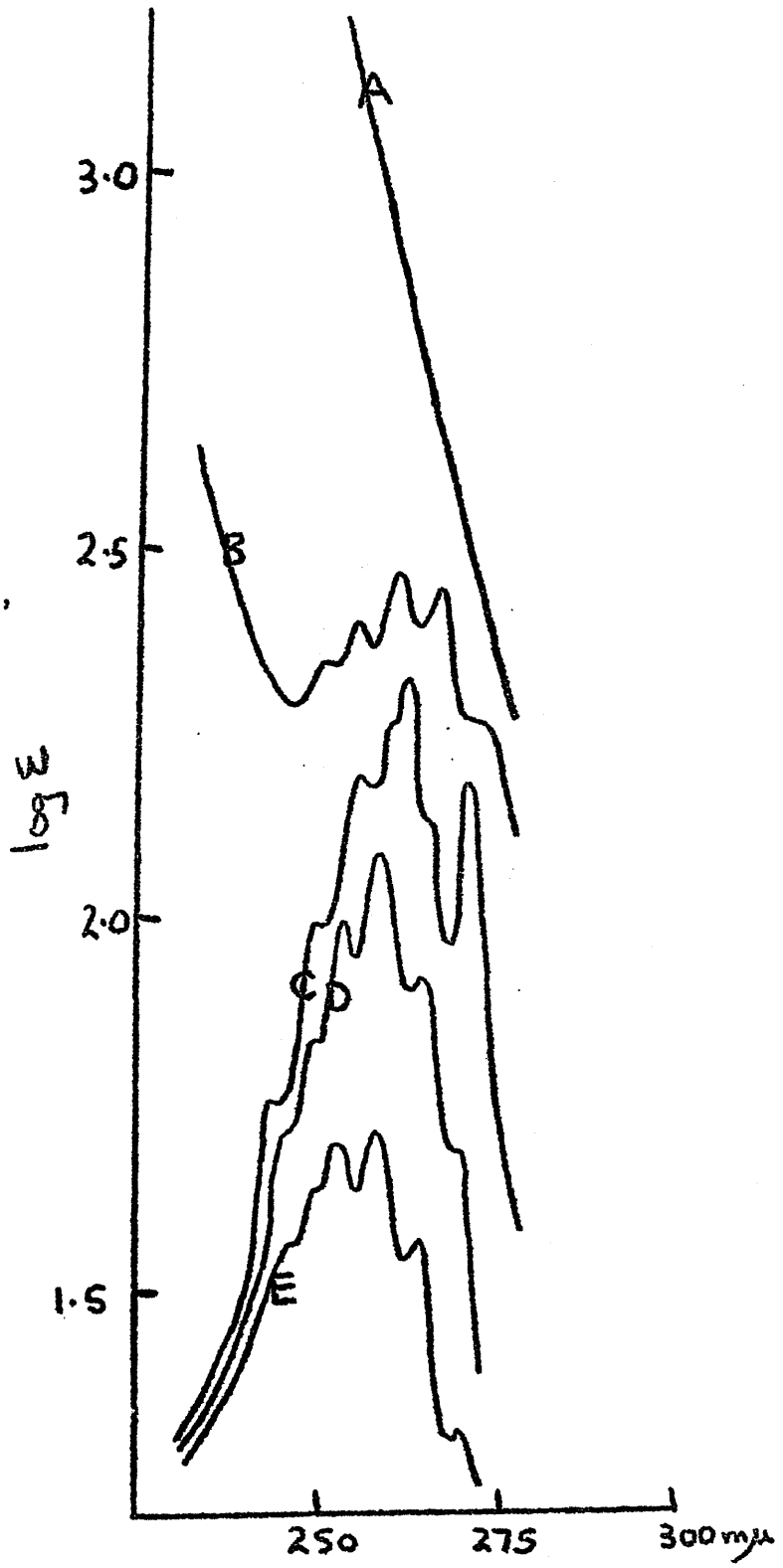


Fig.6.

U.v. spectra:-
A, (145) in ethanol,
B, (158) in ethanol,
C, (201) in ethanol,
D, (202) in ethanol, (add 0.1 to log ε),
E, (198) in ethanol, (add 0.1 to log ε),
F, (160) in ethanol, (add 0.3 to log ε),
G, (159) in ethanol, (add 0.3 to log ε).

Fig.7.

U.v. spectra:-
A, Benzyl bromide in ethanol,
B, Benzyl chloride in hexane, (subtract 0.1 from log ε),
C, Toluene in ethanol,
D, Benzyl alcohol in ethanol, (add 0.1 to log ε),
E, Benzyl acetate in ethanol, (add 0.6 to log ε).



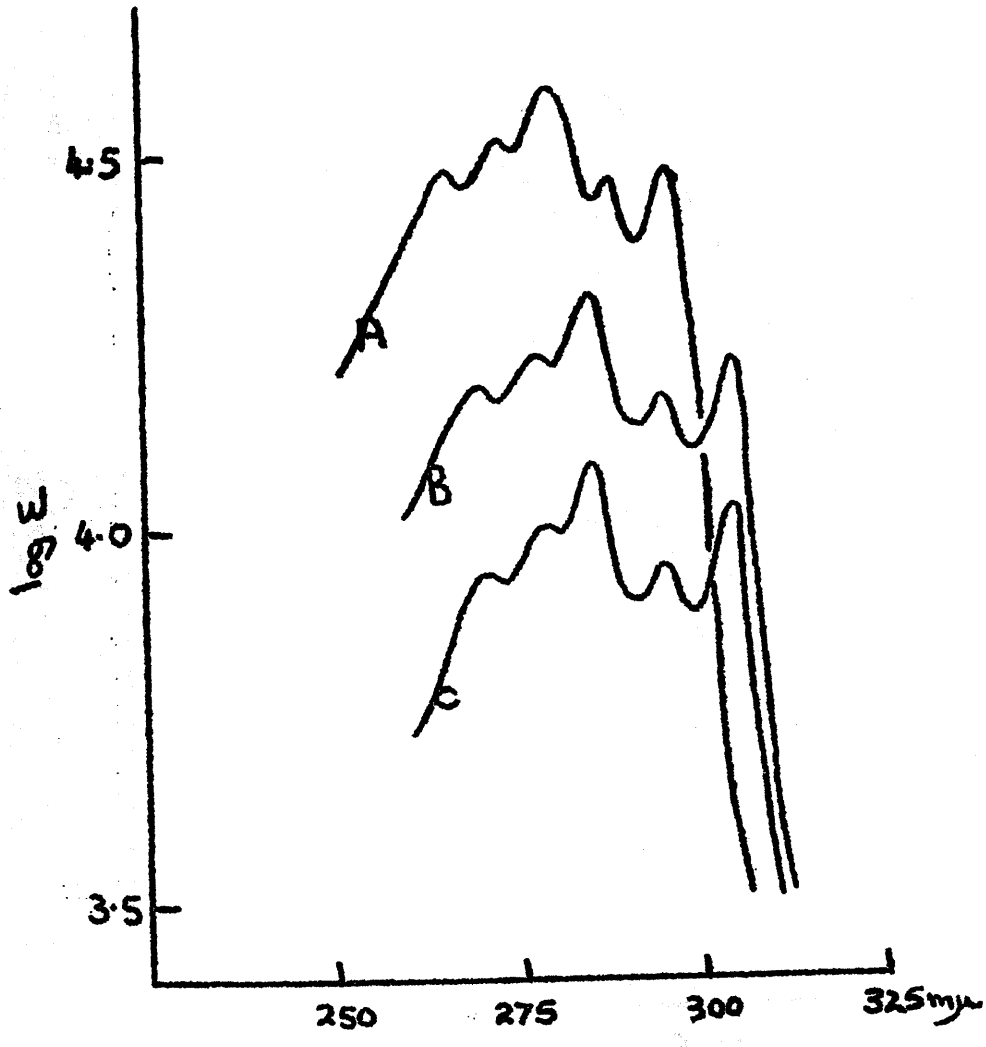


Fig.8.

U.v. spectra:-
A, (71) in ethanol,
B, (132) in hexane, (add 0.1 to log ε),
C, (168) in ethanol, (add 0.3 to log ε).

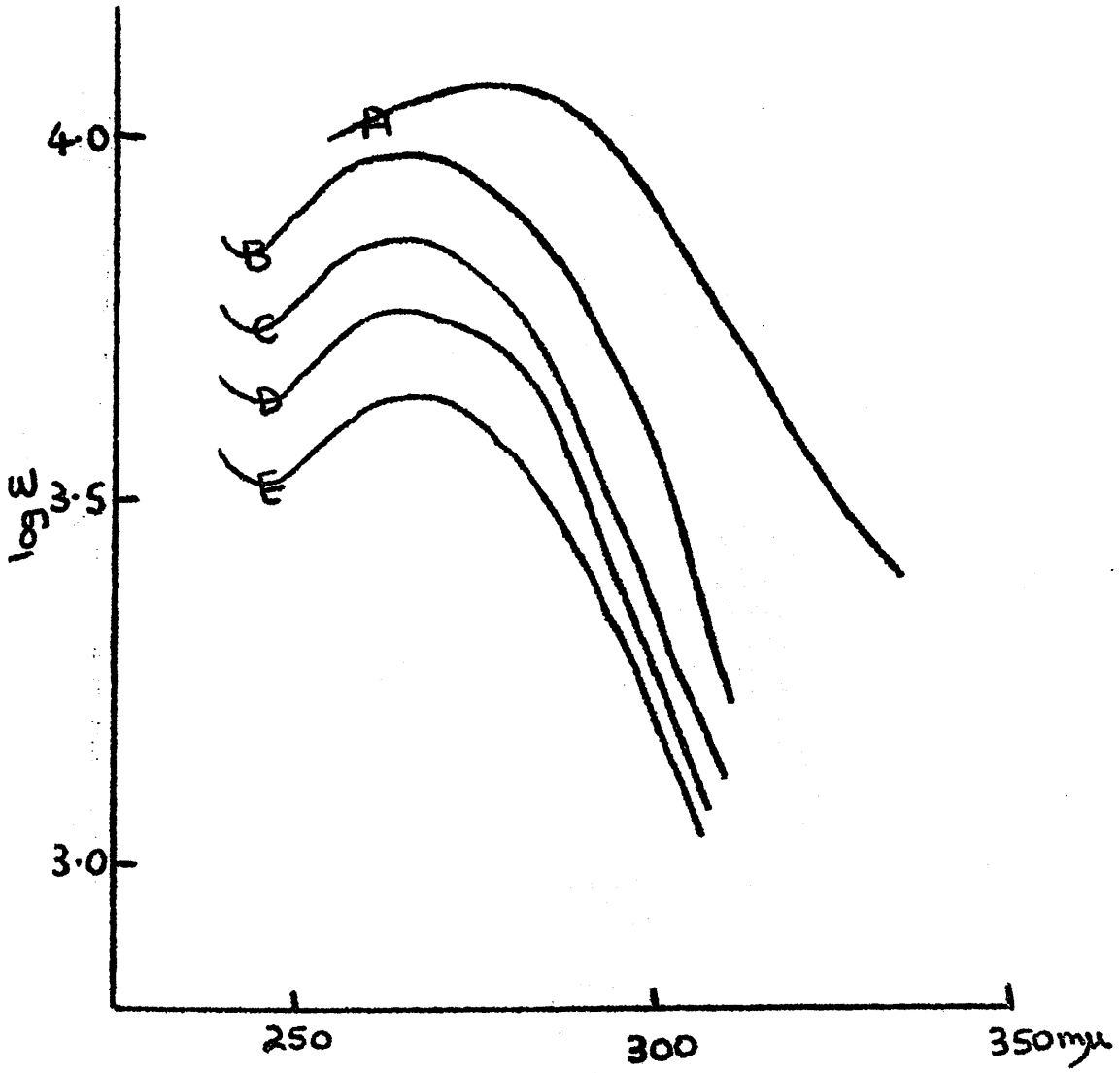


Fig.9.

U.v. spectra:-
A, (130) in ethanol[173],
B, (127) in hexane,
C, (134) in ethanol, (add 0.1 to log ε),
D, (214) in ethanol, (add 0.2 to log ε),
E, (211) in ethanol, (add 0.3 to log ε).

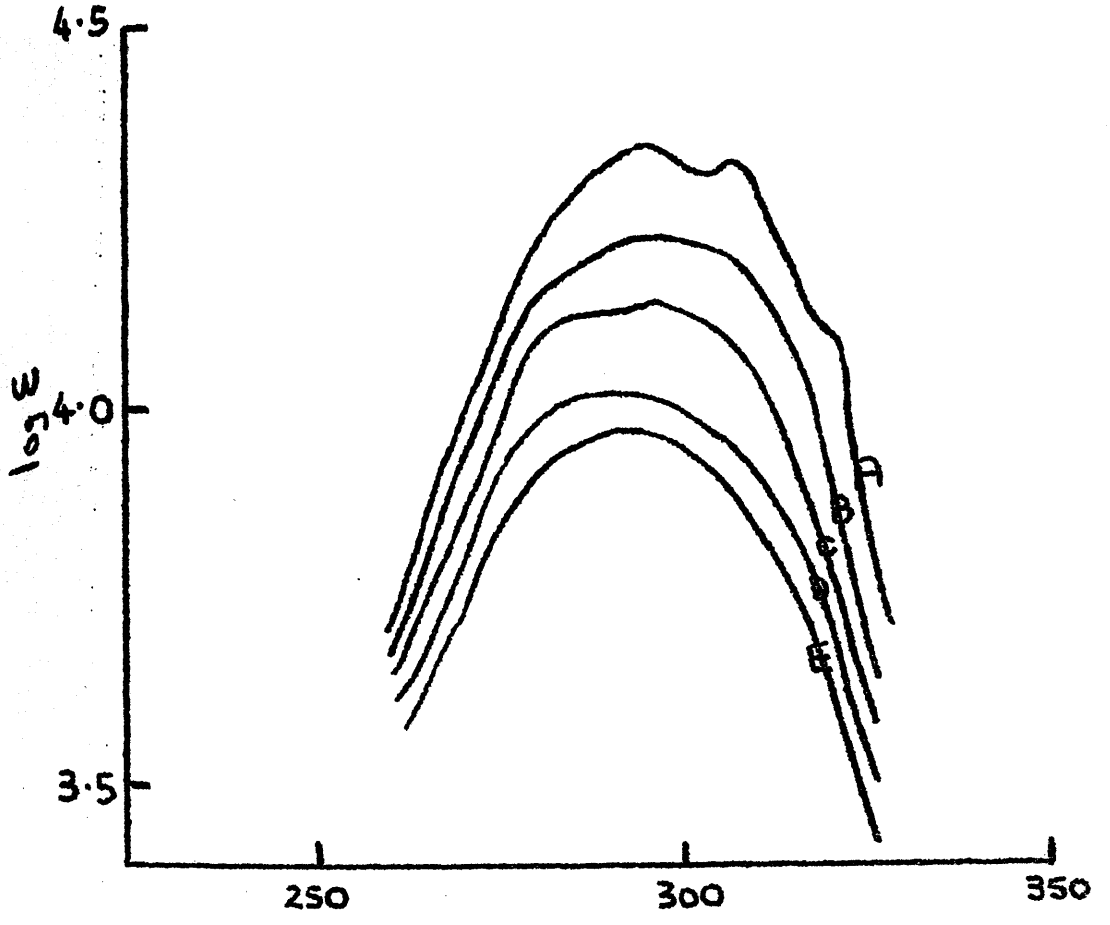


Fig.10.

U.v. spectra:-
A, (129) in ethanol,
B, (128) in ethanol, (add 0.1 to log ε),
C, (135) in ethanol, (add 0.25 to log ε),
D, (215) in ethanol, (add 0.3 to log ε),
E, (212) in ethanol, (add 0.4 to log ε).

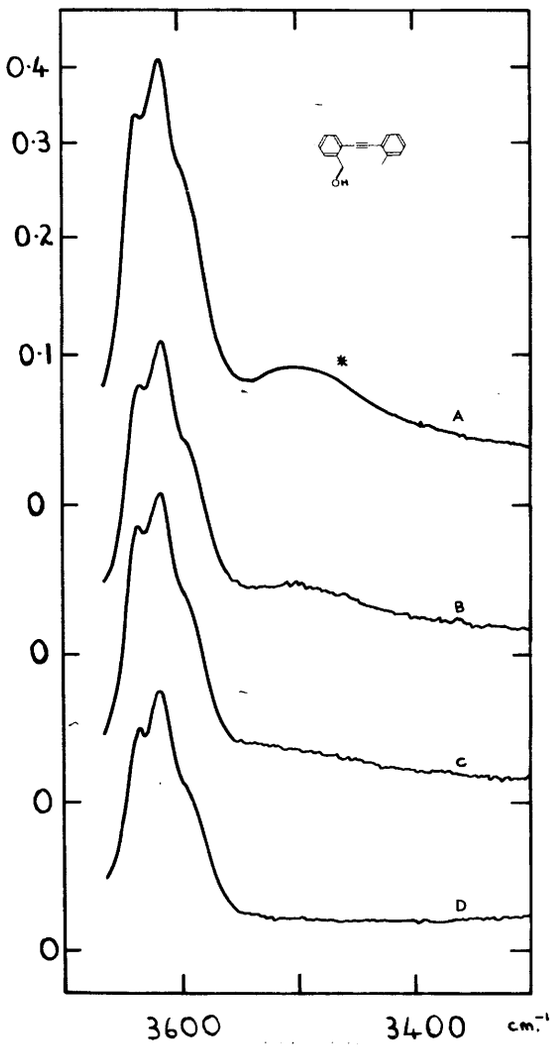


Fig. 11.

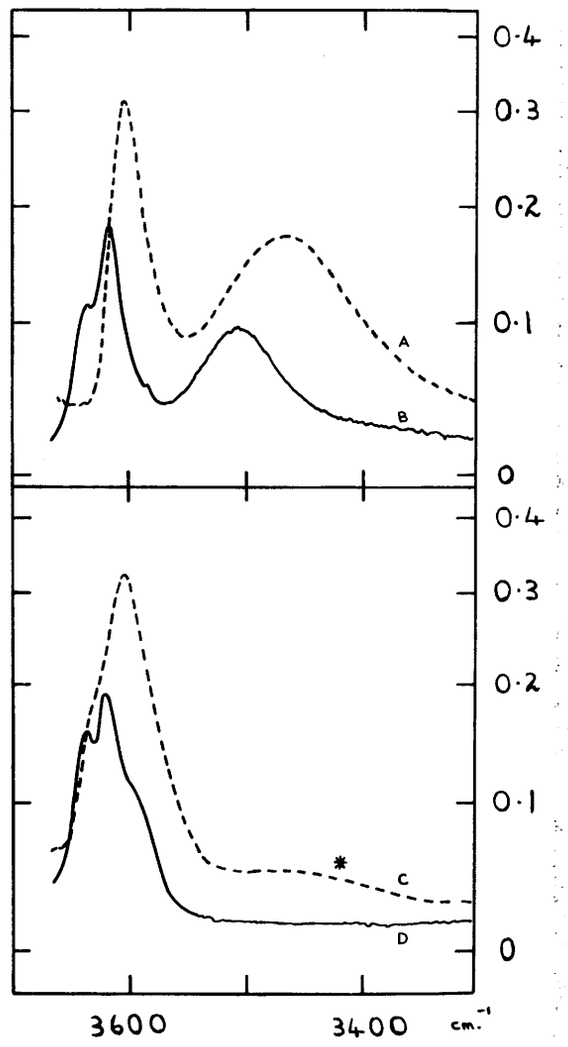


Fig. 12.

Fig. 11.

Hydroxyl stretching absorptions of (201) in CCl_4 solution at various concentrations.

A, 0.051 molar in 2mm. cells.

B, 0.033 molar in 2mm. cells.

C, 0.0034 molar in 2cm. cells.

D, 0.00088 molar in 6cm. cells.

* Inter-molecular association.

Fig. 12.

Hydroxyl stretching absorptions of (145) and (201) in CCl_4 solution and $CHCl_3$ solution.

A, (145) in $CHCl_3$, 0.0065 molar in 5mm. cells.

B, (145) in CCl_4, 0.0013 molar in 2cm. cells.

C, (201) in $CHCl_3$, 0.015 molar in 5mm. cells.

D, (201) in CCl_4, 0.00088 molar in 6cm. cells.

* Inter-molecular association.

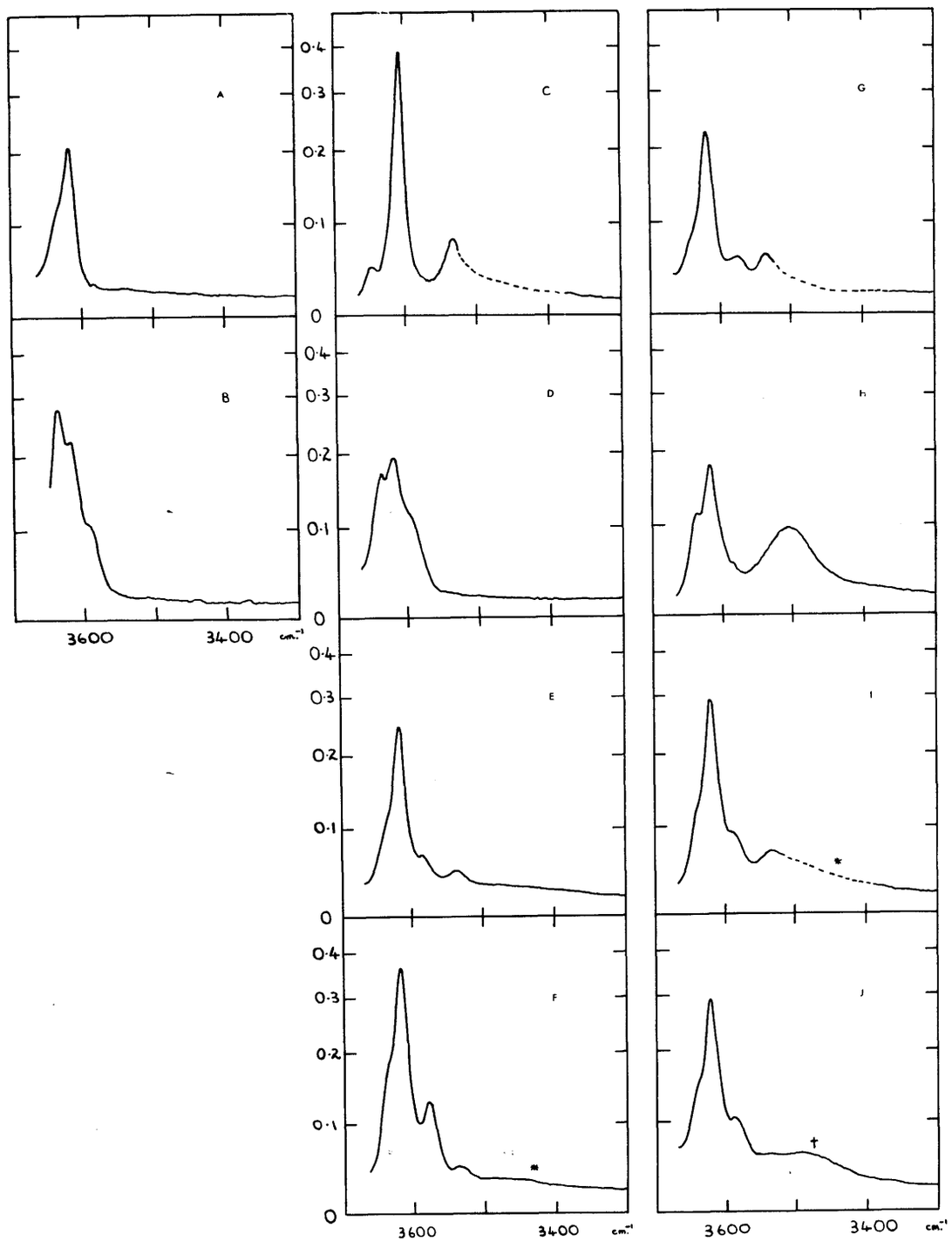


Fig. 13.

Fig. 13.

Hydroxyl stretching absorptions of benzylic alcohols in CCl_4 solution.

A, (216), 0.0015 molar in 2cm. cells.

B, (172), 0.0029 molar in 2cm. cells.

C, (210), 0.0045 molar in 2cm. cells, (full line);
0.0002 molar in 9cm. cells, (broken line).

D, (201), 0.00088 molar in 6cm. cells.

E, (212), 0.0029 molar in 2cm. cells.

F, (211), 0.0043 molar in 2cm. cells.

G, (213), 0.00054 molar in 6cm. cells, (full line);
0.0002 molar in 9cm. cells, (broken line).

H, (145), 0.0013 molar in 2cm. cells.

I, (215), 0.00088 molar in 6cm. cells, (full line);
0.00038 molar in 9cm. cells, (broken line).

J, (214), 0.00076 molar in 6cm. cells.

* Inter-molecular association.

† Inter-molecular association - expected to diminish on further dilution.

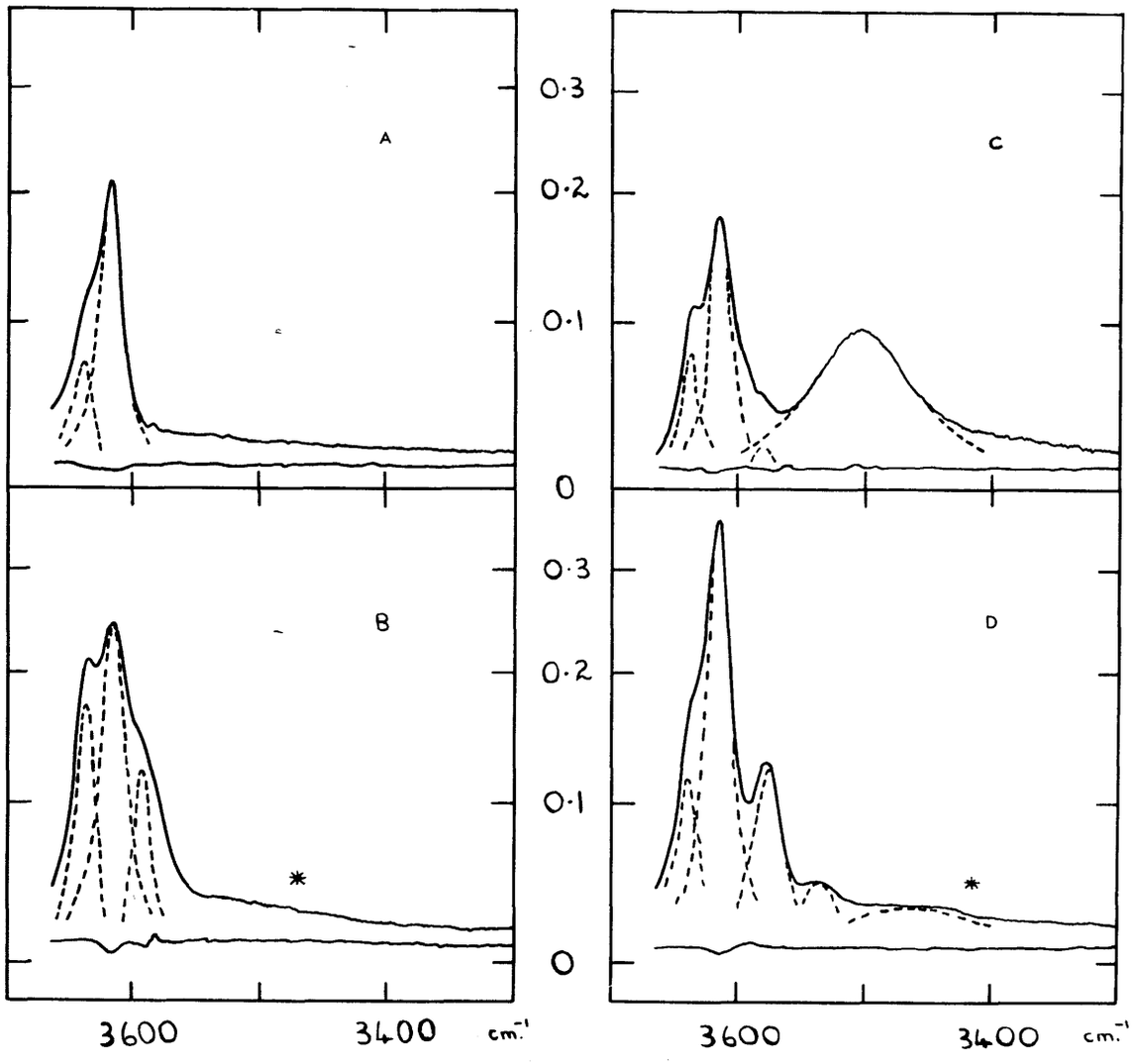


Fig. 14.

Fig. 14.

Hydroxyl stretching absorptions of benzylic alcohols in CCl_4 solution - band construction.

A, (216), 0.0015 molar in 2cm. cells.

B, (201), 0.0034 molar in 2cm. cells.

C, (145), 0.0013 molar in 2cm. cells.

D, (211), 0.0043 molar in 2cm. cells.

* Inter-molecular association.

TABLE 5 - HYDROXYL STRETCHING ABSORPTIONS

OF BENZYLIC ALCOHOLS IN CCl_4 SOLUTION.

Compound	Molarity	Cell length (cm.)	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	Compound
(216)	0.091	0.05	~3635*	—	26	3618†	18	54	~3485[a]	—	12							(216)
(216)	0.0074	0.5	~3635	—	30	3618	18	59	~3485	—	2.4							(216)
(216)	0.0015	2	~3635	—	33	3618	18	62	~3485	—	1.6							(216)
(201)	0.051	0.2	3637*	26	30	3618†	—	38	~3595[b]	—	22	~3495[a]	125	6.2				(201)
(201)	0.033	0.2	3637	26	28	3618	—	41	~3595	—	20	~3495	125	4.4				(201)
(201)	0.0043	2	3637	26	33	3618	—	38	~3595	—	22	~3495	—	2.2				(201)
(201)	0.0034	2	3637	26	29	3618	—	36	~3595	—	19	~3495	—	2.7				(201)
(201)	0.00088	6	3637	26	29	3618	—	33	~3595	—	20	—	—	—				(201)
(210)	0.057	0.2	3648*	—	3	3611†	18	45	3533[c]	—	8	~3490[a]	—	5.3				(210)
(210)	0.0045	2	3648	—	4	3611	18	48	3533	—	8	~3490	—	4.6				(210)
(210)	0.0002	9	3648	—	3	3611	18	48	3533	—	8	—	—	—				(210)
(211)	0.02	0.5	~3635*	—	17	3618†	18	37	3580[d]	—	12	~3535[e]	—	3	~3480[a]	—	2.9	(211)
(211)	0.0043	2	~3635	—	19	3618	18	39	3580	—	12	~3535	—	3	~3480	—	1.4	(211)
(212)	0.027	0.2	~3640*	—	12	3618†	20	41	~3580[d]	—	6	~3535[e]	—	3	~3475[a]	—	2.8	(212)
(212)	0.0029	2	~3640	—	14	3618	20	39	~3580	—	8	~3535	—	5	~3475	—	1.7	(212)
(145)	0.0021	2	3637*	23	41	3617†	28	69	~3580[b]	—	21	3507[f]	90	34	~3340[a]	—	5.6	(145)
(145)	0.0013	2	3637	23	40	3617	28	66	~3580	—	20	3507	90	33	~3340	—	4.3	(145)
(213)	0.0011	2	~3640*	—	19	3618†	20	86	3575[f]	—	17	3535[c]	—	17	~3470[a]	—	6.5	(213)
(213)	0.00054	6	~3640	—	26	3618	20	75	3575	—	15	3535	—	16	~3470	—	5.6	(213)
(213)	0.0002	9	~3640	—	23	3618	20	77	3575	—	16	3535	—	18	~3470	—	~1	(213)
(214)	0.0024	2	~3638*	—	31	3619†	22	68	3585[d]	—	21	~3535[e]	—	11	~3490[a]	—	11	(214)
(214)	0.00076	6	~3638	—	30	3619	22	66	3585	—	22	~3535	—	12	~3490	—	9.4	(214)
(215)	0.0027	2	~3640*	—	25	3618†	23	63	3584[d]	—	21	~3535[e]	—	16	~3480[a]	—	10	(215)
(215)	0.00088	6	~3640	—	24	3618	23	63	3584	—	21	~3535	—	16	~3480	—	8	(215)
(215)	0.00038	9	~3640	—	25	3618	23	63	3584	—	22	~3535	—	16	~3480	—	~2	(215)
(172)	0.041	0.05	3640*	—	53	3620†	—	43	~3592[g]	—	22	~3500[a]	—	5.8				(172)
(172)	0.0029	2	3640	—	47	3620	—	37	~3592	—	16	~3500	—	0.7				(172)

Assignments

* OH "free".

† OH....π (parent aromatic ring).

[a] OH....OH inter-molecular.

[b] OH....π (C≡C).

[c] OH....π (second aromatic ring).

[d] OH....π (C=C) - tentative.

[e] OH....π (second aromatic ring) - tentative.

[f] OH....OH intra-molecular.

[g] OH....Iodine.

TABLE 6 - HYDROXLY STRETCHING ABSORPTIONS

OF (145) AND (201) IN $CHCl_3$ SOLUTION.

Compound	Molarity	Cell length (mm.)	$\nu(cm.^{-1})$	$\nu(cm.^{-1})$	$\nu(cm.^{-1})$
(145)	0.023	2	3607 (36, 86)	3465 (140, 41)	
(145)	0.0065	5	3607 (36, 85)	3465 (140, 42)	
(201)	0.041	2	~3630 (—, 18)	3605 (45, 41)	~3460* (—, 4)
(201)	0.015	5	~3630 (—, 18)	3605 (45, 41)	~3460* (—, 3)

* Inter-molecular association.

Figures in parentheses refer to $\Delta\nu_{\frac{1}{2}}(cm.^{-1})$ and ε values, respectively.

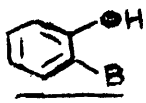
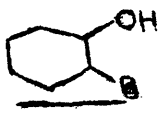
TABLE 7 - DISAPPEARANCE OF INTER-MOLECULAR ASSOCIATION WITH DECREASING CONCENTRATION IN CCl_4 SOLUTION.

Compound	$\nu OH(cm.^{-1})$	Molarity	ε
Mono-ols			
(216)	~ 3485	0.091	12
		0.0074	2.4
		0.0015	1.6
(172)	~ 3500	0.041	5.8
		0.0029	0.7
(201)	~ 3495	0.051	6.2
		0.033	4.4
		0.0043	2.2
		0.0034	2.7
		0.00088	—
(210)	~ 3490	0.057	5.3
		0.0045	4.6
		0.0002	—
(211)	~ 3480	0.02	2.9
		0.0043	1.4
(212)	~ 3475	0.027	2.8
		0.0029	1.7
Diols			
(145)	~ 3340	0.0021	5.6
		0.0013	4.3
(213)	~ 3470	0.0011	6.5
		0.00054	5.6
		0.0002	~1
(214)	~ 3490	0.0024	11
		0.00076	9.4
(215)	~ 3480	0.0027	10
		0.00088	8
		0.00038	~2

TABLE 8 - COMPARISON OF BAND CONSTRUCTION RESULTS VERSUS OBSERVED RESULTS.

	Band Construction			Observed		
Compound	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε
(216)	3640	16	18	~3635	—	33
(216)	3618	18	62	3618	18	62
(201)	3640	17	24	3637	26	29
(201)	3618	18	36	3618	—	36
(201)	3592	16	17	~ 3595	—	19
(145)	3640	17	28	3637	23	40
(145)	3617	19	66	3617	28	66
(145)	3580	—	7	~ 3580	—	20
(145)	3507	90	33	3507	90	33
(211)	3640	16	11	~ 3635	—	19
(211)	3618	18	39	3618	18	39
(211)	3578	26	12	3580	—	12
(211)	3535	—	3	~ 3535	—	3
(211)	3480	—	1	~ 3480	—	1.4

TABLE 9 - POSITION OF HYDROXYL BONDED TO VARIOUS BASIC CENTRES - VALUES IN $\Delta\nu(cm.^{-1})$[170].

B.			
F	20	?	15
OH	44	32	30
Ph	45	23	28
OCH_3	52	36	30
C=C	54	45	40
Cl	63	20	32
Br	82	30	38
I	101	40	46
C≡C	114	41	36
NH_2	—	97	113
$NHCH_3$	?	135	124
$N(CH_3)_2$	244	144	131

SECTION IV

COUPLING OF ETHYNYL COMPOUNDS UNDER HIGH-DILUTION CONDITIONS.

Cupric acetate in pyridine or pyridine-methanol[38,39,40], is now established as a convenient reagent for the Glaser coupling[174-176] of monoterminal acetylenes.

The precise mechanism of the coupling of terminal acetylenes remains to be established, but several schemes have been postulated, e.g.,[177,178]

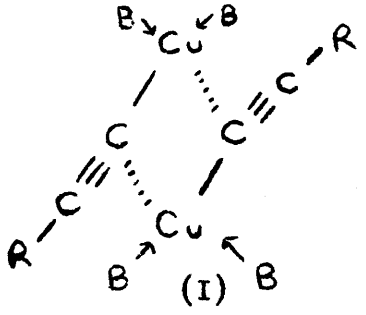
$$R\text{-}C{\equiv}CH \xrightarrow{\text{slow}} R\text{-}C{\equiv}C^- + H^+$$

$$2R\text{-}C{\equiv}C^- + 2Cu^{2+} \xrightarrow{\text{fast}} 2R\text{-}C{\equiv}C\cdot + 2Cu^+$$

$$2R\text{-}C{\equiv}C\cdot \xrightarrow{\text{fast}} R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R$$

The above scheme is supported by the fact that the rate of reaction decreases with decreasing acidity of the acetylenic proton[178].

More recently, Bohlmann and his co-workers[179] have suggested that the coupling reaction involves a cuprous complex, (I),



(I)

(where B is, e.g., pyridine), which is decomposed by cupric ions to the dimer and cuprous ions.

Using cupric acetate, the overall reaction can be written as,

$$2R\text{-}C{\equiv}CH + 2Cu(OAc)_2 \longrightarrow R\text{-}(C{\equiv}C)_2\text{-}R + 2CuOAc + 2HOAc$$

The advantages of pyridine as a solvent are (a) the removal of the acetic acid, hence allowing the reaction to go to completion, and (b) homogeneity, since the cuprous derivative is only seldom precipitated from the reaction mixture, which leads to increased yields. Methanol is employed as co-solvent, since the solubility of the cupric acetate is greatly increased.

No complete systematic study of the use of the cupric acetate-pyridine-methanol reagent appears to have been made, and a brief study of the oxidative coupling of phenylacetylene(77) at various concentrations has been carried out. The relevant points observed now follow, together with a summary of some other observations.

1. Exclusion of water from the reaction does not appear to be essential.
2. A large excess of cupric acetate does not improve the yield.
3. It does not appear to be essential that all the cupric acetate is in solution.
4. Approximately four volumes of ether can be added for high-dilution coupling at a lower reflux temperature, without any precipitation occurring[40].
5. Methanol is best avoided in experiments involving esters, since methanolysis has been encountered[39].
6. A catalytic amount of cupric acetate can be used, provided the cupric ion is regenerated by the passage of oxygen. However, this

procedure is much slower[180].

7. The reagent is not well suited for the coupling of alkynyl compounds; thus, oct-1-yne (217) gave only a 43% yield of the coupled product (218) after a 24 hr. reflux, whereas phenylacetylene(77) gave a 90% yield of (75) after only 1 hr. reflux. Hay has reported[181,182] that these alkyl acetylenes are best coupled using a tertiary amine complex and the cuprous salt, with passage of oxygen.
8. The reaction proceeds well at room temperature, although reaction times longer than those at reflux temperature are necessary.

The cupric acetate-pyridine reagent has also been used extensively[10,38,39,63-69,176,183,184] in the syntheses of macrocyclic acetylenic compounds by the intra-molecular coupling of diterminal diynes, e.g., the preparations of (213; n = 1 and 2)[39], (221; n = 1)[183], (38)[63,184], (45)[66,67], (224; n = 2,3,4,5 and 6)[10] and (225; n = 1 and 2)[39], from (220), (222), (39 and 223), (44), (30) and (226), respectively.

Low reactant concentrations are generally thought to favour any intra-molecular reaction which is in competition with the corresponding inter-molecular processes, and some workers have found[38,39,63,66,67], that the Glaser coupling, when conducted under high-dilution conditions, affords good yields of the lowest cyclic

oligomer* which is sterically feasible. Small amounts of the higher cyclic and linear polymers are also formed. Thus, one ester (220)[39] gave both cyclic monomer (219; n = 1) and dimer (219; n = 2), while a high yield (~88%) of cyclic monomer (221; n = 1) was obtained from another (222)[133]. Only one pure compound, the cyclic dimer (38), could be isolated from the high-dilution coupling of o-diethynylbenzene(39)[33], (see also Section I), and this product was obtained in about the same yield (30%) when the "half-closed" dimer (223) was similarly treated[134].

By contrast, Sondheimer and his colleagues[10] have successfully coupled numerous α,ω-alkadiynes and related compounds at ordinary concentration levels (e.g., ~0.1 molar in pyridine and saturated with respect to copper acetate), but the products are generally complex mixtures of the lower cyclic oligomers. However, similar conditions (e.g., ~0.03 molar in pyridine-methanol, 1:1, by volume, and saturated in copper acetate, ~0.5 molar) were used by the Japanese workers[34-39] in their syntheses of novel cyclic aryl acetylenes, and quite high yields of single compounds resulted in certain cases, e.g., (45) from (44) in 95% yield.

There would therefore appear to be some doubt as to the value of high-dilution techniques in the synthesis of macrocyclic acetylenic compounds by the Glaser coupling reaction. The object

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* See footnote page 27.

of the present short study has been to adduce some quantitative evidence which would reveal any relationship there might be between the initial concentration of diyne and the composition of the coupled product. The diyne chosen was octa-1,7-diyne(30) which has been reported[10] as giving a complex mixture of cyclic dimer, trimer..... hexamer (224; n = 2,3....6) and some long-chain polymers when coupled at ordinary concentrations (cyclic monomer, (224; n = 1) is not sterically feasible). The reaction products were analysed for insoluble long-chain polymers (227) by collecting the precipitate, and for the cyclic and acyclic dimers and trimers by total hydrogenation of the mixture and gas liquid chromatography of the resulting cyclo- and n-hexadecane and tetracosane. This procedure avoids difficulties due to preferential loss incurred either by more conventional analytical procedures such as crystallisation or column chromatography, or by rearrangement and decomposition of the parent acetylenes during gas-liquid chromatography. Further, it permits quantitative comparison with standard hydrocarbons. Cyclic tetramers, pentamers etc., which may have been present, were not detected.

The results of runs at four different concentrations are summarised in Table 10 and illustrated in Fig. 15. In each case the molar concentration of the cupric acetate is four times the initial diyne concentration. A decrease in this concentration is seen to be accompanied by (a) a decrease in the quantity of

insoluble long-chain polymer (227) precipitated from the reaction mixture, (b) a well-defined increase in the proportion of the cyclic dimer (224; n = 2) relative to the cyclic trimer (224; n = 3), and (c) an increase in the proportion of acyclic dimer and trimer to cyclic dimer and trimer, due to incomplete coupling. In the present instance, no attempt has been made to isolate the individual coupled products, but these results[185] would seem to add support to the isolated finding[39], that the relative amounts formed of crystalline cyclic monomer (219; n = 1) and dimer (219; n = 2) changed with the degree of dilution of the starting diyne (220).

Further investigations are desirable, particularly into any effect related to the proportion of Cu^{2+} present, and into the stereochemical requirements of the ethynyl compounds and of any intermediate copper complex, e.g., see above[179]. However, it seems reasonable to conclude that high-dilution conditions favour intramolecular coupling and the formation of cyclic polymers of the lowest ring size feasible.

EXPERIMENTAL. SECTION IV.

Oxidative coupling of phenylacetylene(77) at reflux temperature.

Phenylacetylene(77), titrating[186] as 0.98 active hydrogens per mole, was added to a solution of cupric acetate in pyridine-methanol (1:1, by volume), and the deep-blue reaction mixture heated under reflux for 1 hr., by which time it had turned green. The reaction mixture was cooled, and poured into excess of sulphuric acid (18N) with external cooling. The resulting white suspension was extracted thoroughly with ether, and the combined ethereal extracts washed with water, aqueous sodium bicarbanate solution, aqueous silver nitrate solution (to remove any unchanged phenyl-acetylene) and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a light brown oil, which solidified on cooling. The crude solid diphenyldiacetylene(75) was chromato-graphed on alumina (Brockmann Grade I; 15gm.). Elution with ether-petrol (10%) and recrystallisation from aqueous ethanol gave the pure diphenyldiacetylene(75) as large colourless needles, m.p. 87-88°, mixed m.p. 87-88° with an authentic sample. The compound was also shown to be diphenyldiacetylene(75) by comparison of its i.r. and u.v. spectra and t.l.c. behaviour with an authentic sample.

In the above manner, several coupling reactions of (77) were carried out at the following concentrations:-

(77) (gm.)	Cupric acetate (gm.)	Pyridine (ml.)	Methanol (ml.)	Time at which reaction mixture turned green (min.)	Yield of (75) (%)
1.95	4*	75	75	~30	84
1.94	4*	75[a]	75[a]	~30	93
1.97	5*	75[a]	75[a]	~30	91
1.96	10*	75[a]	75[a]	~30	88
2.3	5.5†	75[a]	75[a]	~30	92
1.99	5.5†	75	75	~30	91
2.0[b]	5.5†	20	20	~10	87
1.98[b]	5.5†	10	10	~5	84

* Anhydrous cupric acetate[187]. † Cupric acetate monohydrate.

[a] Anhydrous solvent.

[b] In this case the reaction mixture was non-homogeneous, not all of the cupric acetate being in solution.

Oxidative coupling of phenylacetylene(77) at room temperature.

A solution of phenylacetylene(77) (1.29gm.) and cupric acetate (3.3gm.) in pyridine (50ml.) and methanol (50ml.) was allowed to stand at room temperature (19°). Aliquots (5ml.) were removed at various intervals, and worked up as before. The yield of diphenyldiacetylene(75) obtained on chromatography, after (a) 1 hr. was 34%, (b) 3 hr. was 48%, (c) 6 hr. was 71% and (d) 24 hr. was 89%.

NOTES. 1. Anhydrous cupric acetate was ~50% more soluble in pyridine than cupric acetate monohydrate.

2. The solubility of cupric acetate in pyridine-methanol (1:1, by volume) was ~4 times greater than in pyridine alone.

Oxidative coupling of oct-1-yne(217).

Oct-1-yne(217) (2.14gm.), titrating[186] as 0.99 active hydrogens per mole, was heated under reflux for 24 hr. in a solution of anhydrous cupric acetate (4gm.) in pyridine (75ml.) and methanol (75ml.). Even after 24 hr., the reaction mixture still gave a precipitate with aqueous silver nitrate solution. Work up as in the coupling of (77), gave (218) as a colourless oil (0.92gm. - 43%), which decomposed on attempted distillation. T.l.c. (silica - petrol as eluent) showed only one spot, R_F 0.85, and the i.r. spectrum (liquid film) showed absorption at ~2150cm.$^{-1}$, ($\nu C{\equiv}C$), but no absorption at ~3300cm.$^{-1}$, ($\nu{\equiv}C{-}H$).

Oxidative coupling of octa-1,7-diyne(60).

A standard solution of cupric acetate was used in all the runs: it consisted of cupric acetate monohydrate (7.52gm.) in pyridine-methanol (1:1, by volume) (100ml.) and was approximately 0.4 molar.

Octa-1,7-diyne(60) (Section V) was distilled and then rigorously purified (1ml. batches) by preparative g.l.c. [Perkin-

Elmer 451 Fractometer, polypropylene glycol column (36" x 1", 20%) at 90°]. The purity of this material was further checked (retention time 8 min.) by analytical g.l.c. on a similar column (46" x 1/5", 25%, 84°, flow rate 60ml./min.).

(a) Preliminary Study. Octa-1,7-diyne(60) (105mg.) was dissolved in the standard copper acetate solution (10.5ml.) contained in a stoppered flask immersed in a water-bath held at 55°. Aliquots (0.5ml.) were removed at frequent intervals, poured into ice-cold sulphuric acid (18N) and then extracted with carbon tetrachloride. The washed and dried extracts were made up to 6ml. with fresh carbon tetrachloride, and the optical densities of the solutions at 3314cm.$^{-1}$, ($\nu\equiv$C-H), determined. The ethynyl content fell rapidly and was virtually zero after 12 hr., (Table 11, Fig. 16).

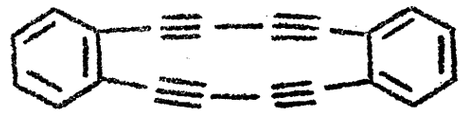
(b) Dilution Study. Each run listed in Table 10 was carried out with a solution as described under (a), after an appropriate volume of the pyridine-methanol (1: 1, by volume) mixture had been added as diluent. After incubation at 55° for 24 hr. in a stoppered flask, the precipitated polymer was collected by filtration and then washed, dried and weighed. It was an off-white powder, not melting below 350°, insoluble in the common organic solvents, and showing weak absorption in the i.r. (KCl disc) at 3294cm.$^{-1}$, ($\nu\equiv$C-H), and was therefore a linear polymer (227). The filtrate was poured into cold sulphuric acid (18N; 25ml.) and extracted thoroughly with ether. The combined ethereal extracts

were washed with water, dried (magnesium sulphate), filtered and the solvent evaporated. The solution of the residue in ethyl acetate was then hydrogenated over 10% palladium on charcoal as catalyst, the uptake of hydrogen approximating to the theoretical value in each case. After filtration, the solution of cyclo- and n-alkanes was concentrated to smaller bulk (~5ml.) and analysed by g.l.c.

(c) Gas-liquid chromatography. A preliminary examination on the Pye Argon Chromatograph [0.5% Apiezon "L" grease on Celite (80-100 mesh)] showed two main peaks which were so widely different in retention times, that isothermal analysis was unsatisfactory, and that some form of temperature programming was desirable. The first peak was proved to be cyclohexadecane by comparison of its retention time with those of cyclododecane and cyclotetradecane. Suitable standards were not available for the second peak, ascribed to cyclotetracosane, but it bore the expected relation to the peaks for the n-C_{24} and n-C_{25} alkanes.

The internal standard method was adopted for the analysis of the hydrogenated product. A known mixture of the n-C_{18} and n-C_{26} alkanes was added to each sample and the solution carefully homogenised and then gas-chromatographed, first at 125° for the cyclo-C_{16} : n-C_{18} ratio, and secondly at 210° for the cyclo-C_{24} : n-C_{26} ratio. The known molar ratio of the n-C_{18} : n-C_{26} mixture then enabled the ratio of the cyclo-C_{16} : cyclo-C_{24} to be calculated. The same procedure was used for the n-C_{16} and n-C_{24} alkanes.

Peak heights were used for the calculations, all peaks being symmetrical. Retention times were as follows: at 125°; 5, 8, and 14 min. for n-C_{16}, cyclo-C_{16}, and n-C_{18} alkanes, respectively; at 210°; 5, 7, and 10 min. for n-C_{24}, cyclo-C_{24}, and n-C_{26} alkanes, respectively.



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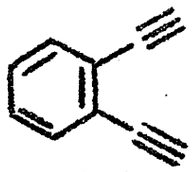

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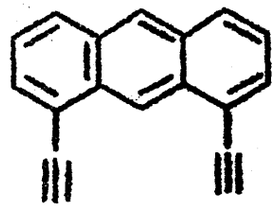

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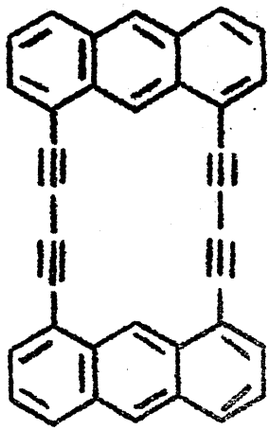

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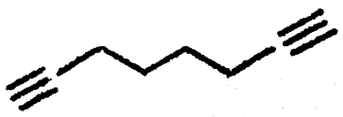

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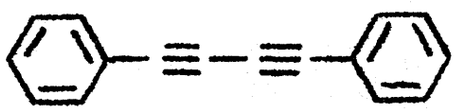

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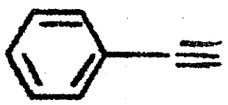
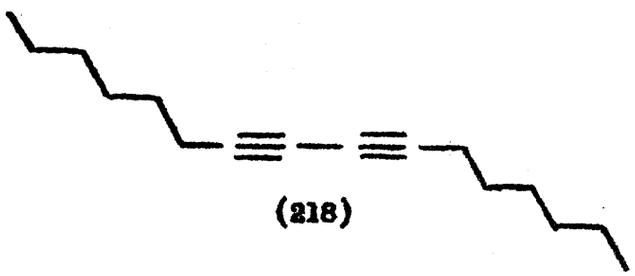


(77)

(217)



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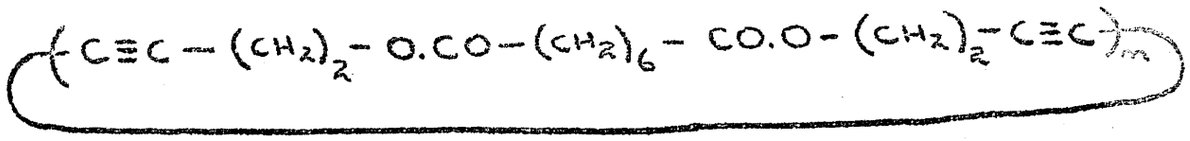

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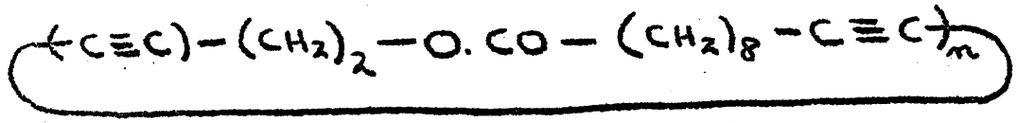

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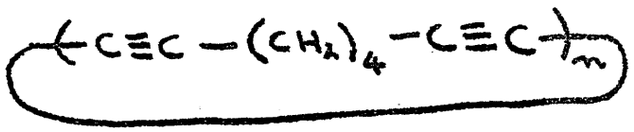

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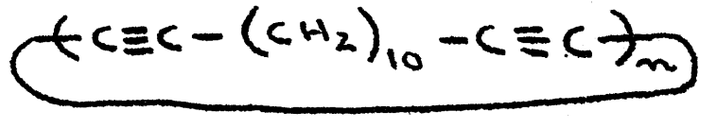

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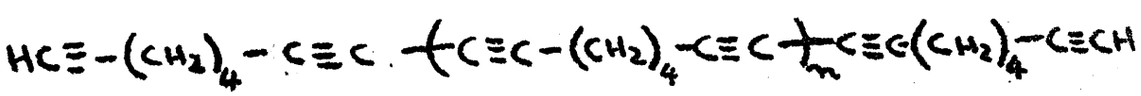

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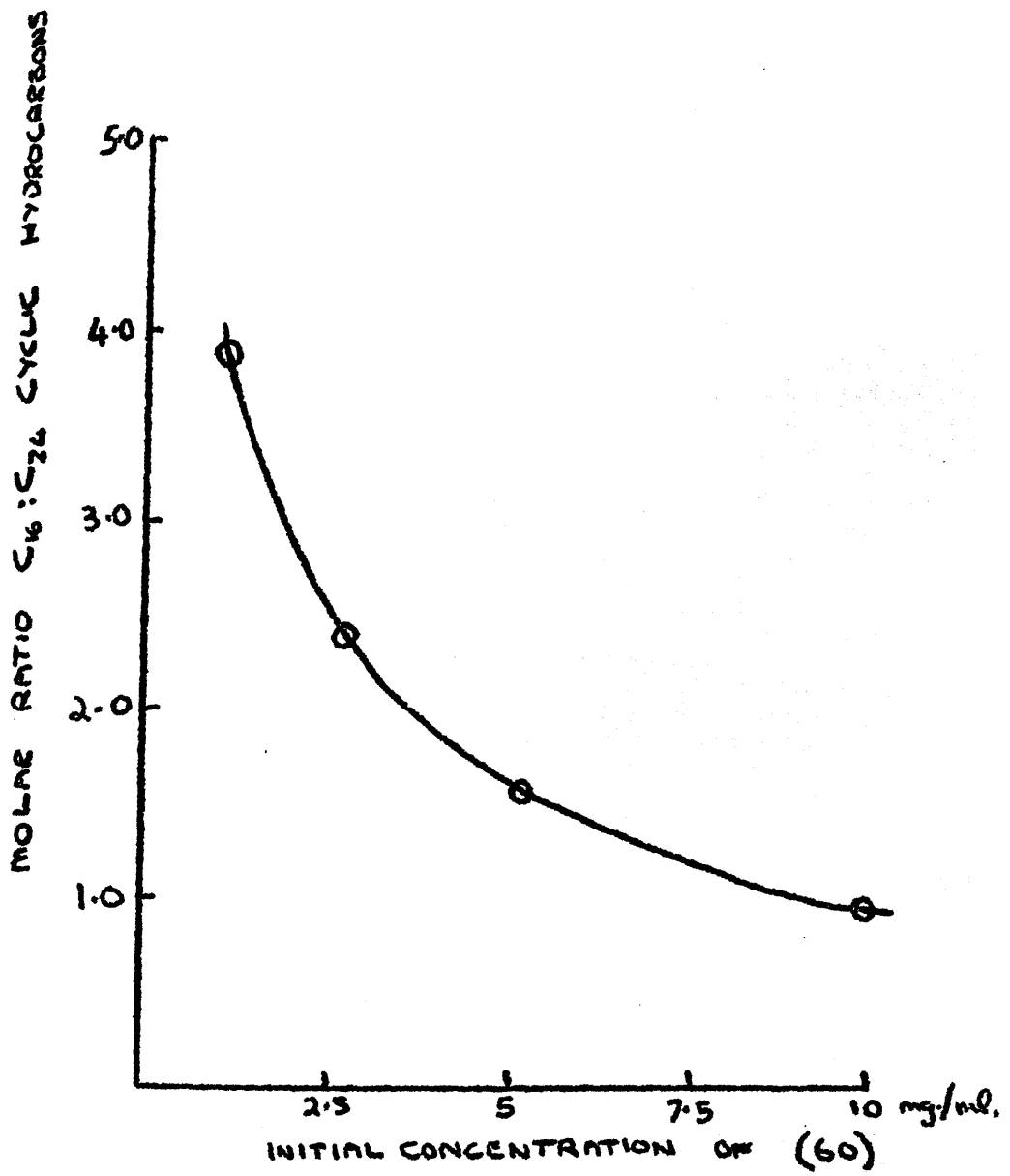


Fig.15.

Molar ratio of the C_{16} cyclic hydrocarbon to the C_{24} cyclic hydrocarbon in relation to initial concentration of octa-1,7-diyne(60).

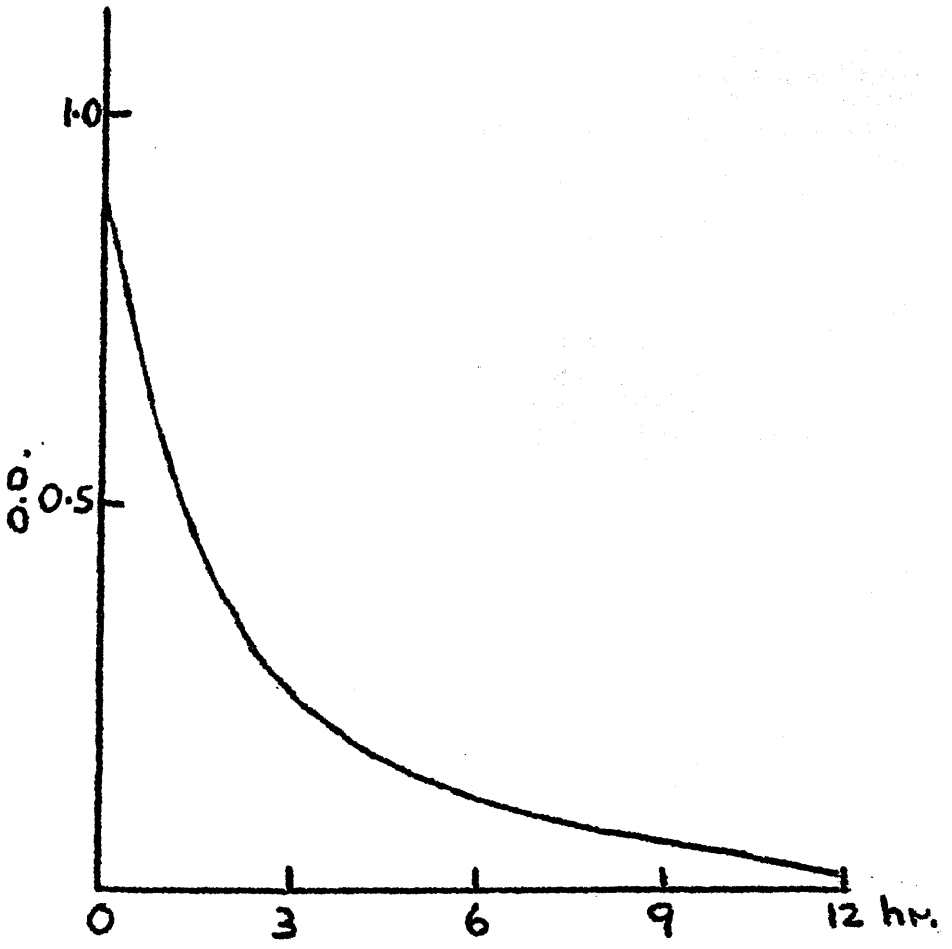


Fig.16.

Disappearance of the 3314cm.$^{-1}$ absorption band in relation to time, in the oxidative coupling of octa-1,7-diyne(60).

TABLE 10 - THE COUPLING OF OCTA-1,7-DIYNE(60) BY CUPRIC ACETATE IN PYRIDINE-METHANOL (1 : 1,BY VOLUME) AT 55°.

Run	Initial diyne concn. (mmole/l.)	Initial $Cu(OAc)_2$ concn. (mmole/l.)	Polymer* (%)	Cyclic dimer † / Cyclic trimer	Acyclic † / Cyclic
1	100	400	55	1.1	‡
2	50	200	43	1.6	0.15
3	25	100	26	2.4	6.7
4	12.5	50	0	3.9	20

* Insoluble precipitate expressed as a percentage of starting diyne; although solution volumes changed, no further ether-insoluble material was obtained after removal of the pyridine.

† Ratio of molar proportions as determined for the corresponding alkanes formed on hydrogenation.
The acyclic alkanes in runs 3 and 4 were in the ratio 6 : 1 :: dimer : trimer.

‡ No acyclic alkanes detected.

TABLE 11 - OPTICAL DENSITY OF THE 3314cm.$^{-1}$ PEAK IN RELATION TO TIME, IN THE OXIDATIVE COUPLING OF OCTA-1,7-DIYNE(60).

Time (hr.)	O.D.
0	0.87
1.5	0.38
3	0.17
5	0.085
12	0.005

SECTION V

HYDRATION OF ACETYLENES.

Hydration of an acetylenic linkage to produce a ketone is probably the best known reaction of this group. The hydration may result from the action of hot acid alone[188], but far more convenient and efficient procedures involve the use of mercuric salts as catalysts. The usual method involves stirring and heating the reactants under reflux in solvents such as ethanol or acetic acid[189-193]. Milder conditions, which circumvent the use of mineral acids and elevated temperatures, employ mercuric acetate in aqueous solvents such as ethanol, methanol, acetic acid, dioxan and ethyl acetate[194-198]. Other mercuric salts which have been successfully employed as catalysts in the hydration of acetylenic linkages include mercuric acetamide[199] and mercuric p-toluenesulphonamide[200]. More recently, ruthenium trichloride[201], molybdic oxide[202], cuprous sulphate[203] and calcium/cadmium phosphate[204] have been employed as catalysts in the hydration of triple bonds.

The mode of addition of a nucleophilic agent to an acetylenic compound, depends on the inductive effect of the groups adjacent to the triple bond.

$$R^1\text{-}C{\equiv}C\text{-}R^2 \xrightarrow{BH} R^1\text{-}CB{=}CH\text{-}R^2$$

In the general case, if R^2 is more electron attracting than R^1, the resulting polarisation is such that the attacking nucleophile adds to the carbon atom furthest from R^2.

Although a great deal of work has been done on the hydration

of triple bonds, the mechanism of the mercury-catalysed hydration is not yet fully understood. It has been suggested that the first step involves a co-ordination complex of the mercuric ion and the acetylene[205-207], and the following scheme has been put forward[208,209],

$$R^1\text{-}C{\equiv}C\text{-}R^2 \xrightarrow{HgX_2} R^1\text{-}\underset{X}{C}{=}\underset{HgX}{C}\text{-}R^2 \xrightarrow{BH} R^1\text{-}\underset{\oplus}{C}{=}\underset{H}{C}\text{-}R^2 + HgX_2$$

(I)

in which the complex (I) reacts with the adding nucleophile in a multi-stage process to yield the product. This scheme follows the above polarising effects.

If the inductive effects of the two groups R^1 and R^2 are very different, then this will lead to the preferential formation of one isomer, and the greater these differences, the greater will be the preponderance of this isomer, e.g., in the extreme case of hydration of an α,β-acetylenic ester, the product is exclusively the β-keto ester. Hydration of a terminal triple bond always produces the methyl ketone, and not the aldehyde, even in cases where the triple bond is flanked by a powerful electron attracting group, e.g., hydration of phenylethynyl ketone(228) produces exclusively 1-phenylpropane-1,2-dione(229)[210], and trifluoromethylacetylene(230) yields trifluoroacetone(231)[211-213]. Of course, the mercuric salt of the ethynyl compound may be the species undergoing hydration, rather than the free ethynyl compound itself, thus reversing the polarising

effect[211-213]. This is supported by the fact that non-mercury-catalysed reactions give the expected products, e.g., addition of diethylamine to (228) gives (232).

In the case of a non-terminal triple bond, where R^1 and R^2 are slightly different, the proportions of the isomeric ketones obtained may be employed as a direct comparison of the polarising influence of the two groups[214-216]. Where R^1 and R^2 are very similar, or where the polar grouping is well insulated from the triple bond, the two possible isomers are usually obtained in equivalent quantities, e.g., the hydration of stearolic acid (233)[188], affords equimolar mixtures of the two possible ketones.

The curious claim by Dobson[217], that hydration of undeca-1,7-diyne(236) did not give the expected equimolar mixtures of undecane-2,7-dione(237) and undecane-2,8-dione(238), but either one or the other, or a non-equimolar mixture, under different conditions, led to a re-investigation and extension of this hydration.

Dobson[217] found that hydration of (236) using (a) the mercuric oxide - boron trifluoride method[218], gave exclusively (237), (b) the mercuric chloride - aniline method[219], gave exclusively (238), and (c) the mercuric sulphate - sulphuric acid method[189-191,220], gave a mixture of (237), (4%), and (238), (51%). However, using a much more precise analytical method, it was found that hydration of (236), under the above hydration conditions, did give the same

mixture of undecane-2,7-dione(237) and undecane-2,8-dione(238) in each case, although the former predominates to an unexpected degree (approximately 2:1). The relevant details of the hydration experiments, together with the preparations of the two diketones (237) and (238), are described below.

Undecane-2,7-dione(237) was synthesised roughly according to Dobson's method[217], starting from cyclohexanone(240), which, on treatment with the Grignard reagent from n-butyl bromide and magnesium, gave 1-n-butylcyclohexan-1-ol(241). Oxidation of (241) with chromium trioxide[221] gave 8-ketodecanoic acid(242). Dobson[217] had claimed that the attempted ketalisation of this acid (242) with only a small excess of ethylene glycol in the presence of p-toluene-sulphonic acid, gave only the ketal-acid (244). However, t.l.c. (silica - chloroform as eluent) revealed four spots, corresponding probably to unchanged keto-acid (242), ketal-acid (244), keto-ester (248) and ketal-ester (243). Infrared spectral examination (Table 12) of this mixture, the keto-acid alone, and reference compounds, all in carbon tetrachloride and ether-carbon tetrachloride (1:4, by volume) solutions, supported the view that all four compounds were present.

The carbon tetrachloride measurements indicated that some ester had been formed [$\nu_{max.}$ 1742cm.$^{-1}$, (νCO); 3623cm.$^{-1}$, (νOH) free; and 3536cm.$^{-1}$, (νOH) intra-hydrogen bonded for $RCO_2CH_2.CH_2.OH$] but that there were also unchanged carboxylic acid and ketonic groups

[$\nu_{max.}$1759sh cm.$^{-1}$, (νCO) for R.CO_2H monomer; 1714cm.$^{-1}$, (νCO) for R.CO_2H dimer and RCOR'; and 3536cm.$^{-1}$, (νOH) for RCO_2H monomer (and for intra-hydrogen bonded $RCO_2.CH_2.CH_2.OH$, as above)]. Confirmation was obtained by the ether-carbon tetrachloride measurements, only two bands in the carbonyl region being observed [$\nu_{max.}$ 1739cm.$^{-1}$, (νCO) for $RCO_2H....OEt_2$ and RCO_2R'; and 1719cm.$^{-1}$, (νCO) for RCOR'].

Presumably Dobson also obtained this mixture of compounds, which probably explains the poor yield of (245) that he obtained on treatment of the ketal-acid (244) with ethereal methyllithium.

The keto-acid (242) was therefore treated with a large excess of ethylene glycol and converted into the glycol ester of 6,6-ethylenedioxydecanoic acid(243). Base hydrolysis of this ester (243) gave the free acid (244) which, by reaction with methyllithium gave 7,7-ethylenedioxyundecan-2-one(245). However, acidification of the salt obtained on base hydrolysis of (243) did not give reproducible results, and often resulted in hydrolysis of the acid-sensitive ketal to regenerate some of the keto-acid (242). It was found that a better method of obtaining (245) was to hydrolyse the ester (243) with lithium hydroxide, and isolate the lithium salt (246) by evaporation of the water. The salt (246) was then subjected to methyllithium treatment to give (245). Acid hydrolysis of the ketal (245) furnished the required undecane-2,7-dione(237).

For the second diketone (238), cyclohexanone(240) was acylated using boron trifluoride as catalyst in the usual way[222], to give

2-n-butyrylcyclohexan-1-one(249), which was subjected to base-catalysed fission[223] to yield 7-ketodecanoic acid(250). By procedures cognate to those above, this acid was converted into undecane-2,8-dione(238). A mixture of these two crystalline diketones, (237) and (238), liquefied. T.l.c. did not separate the two diketones, and mixtures of them under various conditions always produced only one spot.

Satisfactory g.l.c. separation of synthetic mixtures of these two closely-related diketones proved predictably difficult. A wide variety of both non-polar (Apiezon "L" grease and S.E.30) and polar (polyethylene glycol adipate, Q.F.1 and Carbowax) phases gave no indication of any separation. Attempted separation of the two corresponding bis-ethylene ketals, (247) and (254), on Apiezon "L" grease was more successful, but still inadequate for quantitative purposes. Success in separating the diketones was achieved by means of the high resolution available from a polypropylene glycol-coated capillary column (50 metre). Under these conditions there was a difference of approximately one minute in retention time, which proved adequate for quantitative measurements involving peak triangulation. The results of this process applied to weighed mixtures of the two diketones gave a satisfactory linear peak-area/composition relationship. This technique was then applied to the products of hydration of undeca-1,7-diyne(236), prepared from tetramethylene bromide(235), via octa-1,7-diyne(60) in the usual

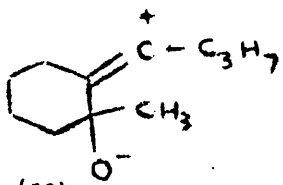
way[224].

The hydrations, first on octa-1,7-diyne(60) as a model compound, and then on undeca-1,7-diyne(236), were successfully carried out using mercuric sulphate - sulphuric acid[189-191,220], boron trifluoride - mercuric oxide[218], mercuric chloride - aniline[219], and mercury-impregnated polystyrene resin[225]. An attempted hydration using ruthenium trichloride in hydrochloric acid[201], unexpectedly furnished a complex mixture, which will be discussed later.

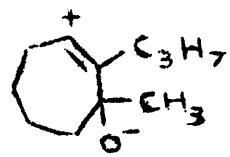
Analysis by g.l.c. of the mixtures derived from the above four hydration techniques showed that within the limits of experimental error the proportions of 2,8- to 2,7-diketone (238 and 237, respectively) were the same in all the products. (Table 13). This was certainly the expected result and gainsaid the indications of the earlier work[217]. Less expected, however, was the finding that the proportions of the two diketones were not 50:50 but consistently 70:30 in favour of the 2,7-diketone(237). It is hardly likely that the hydration of the central triple bond of the initially-produced undeca-7-yn-2-one(261) would be influenced by an inductive effect of the carbonyl group transmitted through four methylene groups; in any case such an effect would favour the formation of the 2,8-dione(238), (it is relevant that hydration of stearolic acid produces the expected equimolecular mixture of the two keto-acids)[188].

More plausible is the operation of some proximity effect, which

in the case of undeca-7-yn-2-one(261) could lead to charge-transfer intermediates of the type (II) or (III).

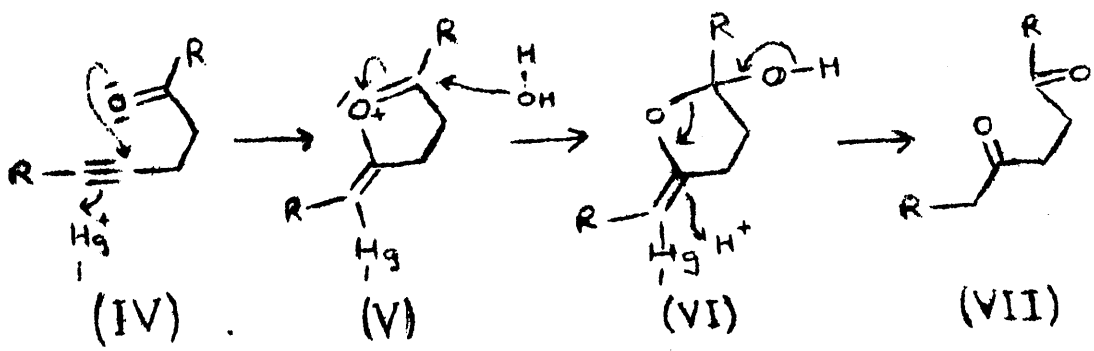


(II)



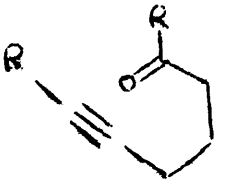
(III)

Nucleophilic attack on these structures would lead to the 2,8-(238) and 2,7-dione(237), respectively. It is difficult, however, to rationalise any favouring of the latter intermediate which would give rise to the observed preferred direction of hydration. More detailed speculation would seem to be unfruitful at this stage, in view of the present unsatisfactory state of knowledge of the detailed mechanism of these mercuric-catalysed hydrations. However, since the publication of these results[226], Stork and Borch[229] have reported that hydration of γ-acetylenic ketones of type (IV), produce exclusively the diketone (VII), via the proposed five-membered ring intermediates, (V and VI).

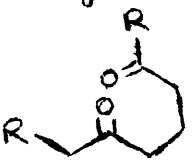


(IV) (V) (VI) (VII)

They also reported that hydration of δ-acetylenic ketones, e.g., (VIII), produce exclusively diketones of type (IX). They propose a six-membered ring intermediate, and find that the hydration of the δ-ketones is faster than the γ-ketones.

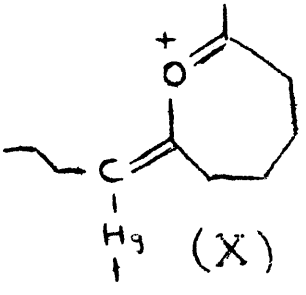


(VIII)

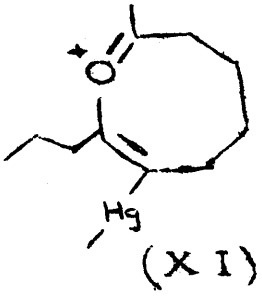


(IX)

If this type of mechanism is applied to hydration of (236), then the initially formed undeca-7-yn-2-one(261), would hydrate via the intermediates (X) and (XI);



(X)



(XI)

structure (X) is perhaps more favoured than (XI), accounting for the preferential formation of the 2,7-diketone(237) rather than the 2,8-isomer, (238).

As mentioned earlier, attempted hydration of octa-1,7-diyne(60) using ruthenium trichloride in hydrochloric acid[201], gave unexpected results. The i.r. spectrum showed, [in addition to unchanged starting material (~3300cm.$^{-1}$ and ~2120cm.$^{-1}$), and the expected carbonyl absorption (~1710cm.$^{-1}$)], absorption at ~2050cm.$^{-1}$ and

~1980cm.$^{-1}$, the region where allenes absorb, and at ~1350cm.$^{-1}$ and ~1300cm.$^{-1}$, corresponding to carbon-carbon double bond stretching.

However, phenylacetylene(77) on similar treatment with ruthenium trichloride in hydrochloric acid, did give the expected acetophenone(177) in good yield.

A simple alk-1-yne, oct-1-yne(217), was therefore subjected to the ruthenium trichloride-hydrochloric acid reagent. Again the i.r. spectrum of the crude reaction product showed absorption due to terminal triple bond (~3300cm.$^{-1}$ and ~2130cm.$^{-1}$), ketone (~1720cm.$^{-1}$), allene (~2070cm.$^{-1}$ and ~1980cm.$^{-1}$) and carbon-carbon double bond (~1620cm.$^{-1}$). A g.l.c. study showed five peaks. For comparison purposes, octan-2-one(255) was synthesised by oxidation of octan-2-ol(256), and was shown to be present (~40%) by co-injection. Unchanged acetylene (217) (~20%) was also present, and could be removed from the crude reaction mixture by treatment with aqueous silver nitrate. The acetylene (217) was therefore not being formed from the allene during gas-chromatography. The two peaks at the beginning of the trace, retention times 2.2 min. (~5%) and 2.9 min. (~5%), may be allenes and/or decomposition products. The last peak in the g.l.c. trace (~30%) had a retention time of the correct order for a compound of structure (257), formed by simple hydrogen chloride addition to the acetylene (217). Therefore, oct-1-yne(217) was subjected to the treatment of Backer and Blass[227], for the addition of hydrogen chloride to the triple

bond. No compound of structure (257) was isolated, the only compounds obtained being the ketone (255) and unchanged acetylene (217).

Oct-1-yne(217) was then treated with (i) hydrochloric acid, (ii) ruthenium trichloride trihydrate in ether, (iii) ruthenium trichloride in water, (iv) ruthenium trichloride trihydrate in ether which had been saturated with hydrogen chloride gas and (v) anhydrous ruthenium trichloride in ether which had been saturated with gaseous hydrogen chloride. The results are summarised in Table 14.

In conclusion, it would appear that (i) ruthenium trichloride in ether saturated with hydrogen chloride gas is a much more efficient hydration catalyst than the reported method[201], (ii) under the reported conditions[201] (and not under any of the other conditions investigated), side reactions occur, although the exact nature of the products, and the mechanism of their formation, is by no means clear.

Further studies with carefully chosen acetylenes, e.g., benzylacetylene(232), and use of g.l.c. combined with mass spectrometry, and use of preparative g.l.c., could perhaps shed additional light on the nature of the reaction products.

EXPERIMENTAL SECTION V.

Preparation of tetramethylene bromide(235).

Tetrahydrofuran(234) (360gm.) in hydrobromic acid (48%; 2000ml.) was heated under reflux for 4 hr., and the resulting black tarry reaction mixture steam distilled. The colourless dibromide layer was separated, washed with concentrated sulphuric acid, then water, and dried over calcium chloride. After decantation, distillation of the oil gave tetramethylene bromide (235) (782gm. - 72%), as a clear mobile oil, b.p. 72-74°/14mm. n_D^{20} 1.5186. (Fried and Kleene[228] give b.p. 76°/11mm.).

Preparation of octa-1,7-diyne(60)[229].

Sodium (1gm.) was added to ferric nitrate (1.5gm.) in liquid ammonia (1800ml.) and the reaction mixture stirred for 30 min., until the initial deep blue coloration was replaced by a white suspension of sodamide. More sodium (117gm.) was then slowly added, and when the reaction mixture had once again turned white, acetylene was passed through the reaction mixture, until a black coloration was observed (after ~5 hr.). Tetramethylene bromide (235) (270gm.) in dry ether (500ml.) was then added over 1 hr. with stirring and cooling, (alcohol-carbon dioxide, -40°). Ether (100ml.) was added and stirring was continued overnight, during which time most of the ammonia evaporated. Solid ammonium chloride was added to decompose the excess sodium acetylide, and then ice-

water containing ammonium chloride was cautiously added. The ether layer was washed successively with dilute sulphuric acid (2N), saturated aqueous sodium carbonate solution and water, dried (magnesium sulphate) and filtered. The ether was removed through a column, and fractional distillation of the residual oil gave octa-1,7-diyne(60) (7.3gm. - 54%) as a clear, mobile oil, b.p. 38-40°/14mm., n_D^{23} 1.4504. (Bader, Cross, Heilbron and Jones[229] give b.p. 93-95°/190mm., n_D^{18} 1.4521). The i.r. spectrum (CCl_4 solution) showed absorption at 3314cm.$^{-1}$ ($\nu \equiv C-H$ stretch) and estimation of the ethynyl content[136] gave 1.95 active hydrogens per mole. G.l.c. [10% Apiezon "L" grease on Celite (80-100 mesh) at 50°] showed one main peak (retention time, 10 min.) (~95%), plus two minor impurities, (retention times, 23 min. and 34 min.).

Preparation of undeca-1,7-diyne(236)[224].

Sodium (1.25gm.) was added to liquid ammonia (50ml.) containing ferric nitrate (~20mg.), and the solution stirred until the initial deep blue coloration had been replaced by the white suspension of sodamide. Octa-1,7-diyne(60) (5.3gm.) in dry ether (10ml.) was added over 10 min. with stirring and cooling (alcohol-carbon dioxide, -40°). Stirring was continued for 2 hr. and n-propyl iodide (10.25gm.) in dry ether (10ml.) was slowly added. The reaction mixture was stirred at -40° for 6 hr. The ammonia was allowed to evaporate overnight, and solid ammonium chloride was

added, followed by ice-water containing ammonium chloride. The ether layer was washed successively with water, dilute sulphuric acid (2N), aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. The ether was evaporated, and fractional distillation of the residual oil gave undeca-1,7-diyne(235) (3.1gm. - 42%) as a clear, mobile liquid, b.p. 85-87°/15mm., n_D^{20} 1.4571. (Raphael and Sondheimer[224] give b.p. 97-99°/23mm., n_D^{20} 1.4573). The i.r. spectrum (liquid film) showed absorption at ~3320cm.$^{-1}$ ($\nu \equiv C-H$ stretch) and titration of the ethynyl group[136] showed 1.04 active hydrogens per mole. G.l.c. [10% Apiezon "L" grease of Celite (80-100 mesh) at 100°, flow rate 45ml./min.], showed a very large peak (retention time, 12 min.) corresponding to (235), plus very small peaks corresponding to propyl iodide and octa-1,7-diyne(60), and a small peak (retention time, 1 hr. 58 min.), thought to be due to the C_{14} di-substituted hydrocarbon (258).

Preparation of 1-n-butylcyclohexan-1-ol(241)[217].

The Grignard reagent from n-butyl bromide (137gm.) and magnesium (24.3gm.) in dry ether (1500ml.) was prepared in the usual manner. Cyclohexanone(240) (84gm.) in dry ether (100ml.) was added dropwise to the Grignard reagent over 5 hr. with ice bath cooling, never allowing the temperature to exceed 5°. After decomposition of the complex with ice and dilute hydrochloric acid,

the ether layer was separated and extracted with aqueous sodium bisulphite solution (to remove any unchanged ketone), washed with water, dried (magnesium sulphate) and filtered. After removal of the ether , distillation of the residual oil gave 1-n-butylcyclohexan-1-ol(241) (86.6gm. - 65%) as a clear, mobile oil, b.p. 98-100°/14mm., n_D^{24} 1.4527. (Signaigo and Cramer[230] give b.p. 88-91°/7mm., n_D^{20} 1.4648). The i.r. spectrum (liquid film) showed absorption at ~3350cm.$^{-1}$ (ν O-H stretch), and was devoid of any absorption bands in the region of 1700cm.$^{-1}$ (ν C=O).

Preparation of 6-ketodecanoic acid(242)[217].

1-n-Butylcyclohexan-1-ol(241) (18gm.) in glacial acetic acid (750ml.) was treated with chromic anhydride (56gm.) in small portions with vigorous stirring. Stirring was continued for 24 hr., when the reaction mixture was concentrated under reduced pressure (to ~250ml.), and water (500ml.) added. Extraction with ether, followed by washing the ethereal extract twice with water, and extraction with aqueous sodium hydroxide solution (37.5gm. in 500ml.) led to an aqueous solution of the sodium salt of the acid. This extract was acidified with concentrated hydrochloric acid, and extracted with ether in a continuous ether extraction apparatus. Drying (magnesium sulphate) and evaporation, gave a crude solid, which was distilled (b.p. 135-145°/0.1mm.) and recrystallised from petrol to give 6-ketodecanoic acid(242) (6.7gm. - 31%) as

needles, m.p. 41-42°. (Found: C, 64.25; H, 9.90. $C_{11}H_{18}O_3$ requires C, 64.5%; H, 9.75%). (Dobson[217] gives b.p. 123-125°/0.02mm. and Yoshioka[231] gives m.p. 42°). The semicarbazone was obtained as needles, m.p. 159° from methanol. (Yoshioka[231] gives m.p. 159°). T.l.c. of the keto-acid (242), (silica - chloroform as eluent) showed only one tailing spot, $R_F \sim 0.1$. The i.r. spectrum (nujol mull) was typical of a carboxylic acid, showing a broad absorption band at ~3000cm.$^{-1}$ (νO-H), and absorption at ~1730cm.$^{-1}$ (νC=O). The quantitative i.r. absorption data in various solvents (Table 12) confirm that the compound is a keto-acid.

Attempted preparation of 3,6-ethylenedioxydecanoic acid(244)[217].

6-Ketodecanoic acid(242) (3.75gm.), ethylene glycol (2gm.) and p-toluenesulphonic acid (60mg.) were stirred and heated under reflux for 3 hr. in anhydrous benzene (90ml.), with automatic water separation. The benzene solution was cooled, washed with aqueous sodium acetate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a clear oil (4.5gm.), which on attempted distillation at 2×10^{-4}mm. resulted in partial decomposition. T.l.c. (silica - chloroform as eluent) showed four spots, $R_F \sim 0.1$ tail, ~0.3 tail, 0.45 and 0.55. The i.r. spectrum (Table 12) showed absorption characteristic of an acid, a ketone and an ester, and the mixture probably consists of unchanged keto-acid (242), ($R_F \sim 0.1$), ketal-acid (244), ($R_F \sim 0.2$),

keto-ester (243), (R_F 0.45) and ketal-ester (243), (R_F 0.58).

Preparation of 2-hydroxyethyl 3,6-ethylenedioxydecanoate(243).

6-Ketodecanoic acid(242) (3.75gm.), ethylene glycol (18.5gm.) and p-toluenesulphonic acid (30mg.) were stirred and heated under reflux for 3 hr. in anhydrous benzene (90ml.) with automatic water separation. The cooled benzene solution was shaken with anhydrous potassium carbonate, washed with aqueous sodium acetate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the benzene gave (243) (5.12gm. - 93%) as a clear viscous oil which could not be distilled. T.l.c. (silica - chloroform as eluant) showed only one spot, R_F 0.55, and the i.r. spectrum (Table 12) was devoid of absorption due to ketonic or carboxylic acid carbonyls, but showed absorption characteristic of an ester.

Preparation of 3,6-ethylenedioxydecanoic acid(244).

The ester (243) (5.74gm.) was heated under reflux in aqueous sodium hydroxide solution (0.6gm. in 30ml.) for 2 hr. After cooling, and ether extraction, the aqueous reaction mixture was acidified carefully with dilute sulphuric acid to pH6, with ice-salt cooling. The reaction mixture was extracted thoroughly with ether, and the combined ethereal extracts washed thoroughly with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave (244) (2.04gm. - 89%) as a pale yellow oil, which

could not be distilled. T.l.c. (silica - chloroform as eluent) showed essentially only one spot, $R_F \sim 0.2$ tail. The i.r. spectrum (Table 12) showed absorption typical of a carboxylic acid function, but none characteristic of a ketone or ester.

Preparation of lithium 6,6-ethylenedioxydecanoate(246).

The ester (243) (2.2gm.) was heated under reflux in aqueous lithium hydroxide solution (0.4gm. in 25ml.) for 2 hr. After cooling, and ether extraction, the aqueous reaction mixture was evaporated to dryness under reduced pressure, to give the lithium salt (246) (2.0gm. - 96%) as a colourless solid which did not melt below 350°.

Preparation of 7,7-ethylenedioxyundecan-2-one(245).

(a) From the acid (244). To a solution of the acid (244) (420mg.) in anhydrous ether (5ml.) was added ethereal methyllithium (0.45 molar; 10ml.). The reaction mixture was heated under reflux for 1 hr., cooled, and water was added. The ether layer was washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave (245) (390mg. - 94%) as a clear viscous oil, b.p. 99-102°/10^{-4}mm., n_D^{24} 1.4552. (Dobson[217] gives b.p. 99-101°/4 x 10^{-4}mm., n_D^{25} 1.4550). T.l.c. (silica - chloroform as eluent) showed only one spot, R_F 0.8. The i.r. spectrum (CCl_4 solution) showed ketonic absorption at 1721cm.$^{-1}$.

(b) From the lithium salt (246). To a suspension of the lithium salt (246) (2gm.) in anhydrous ether (25ml.) was added ethereal methyllithium (0.41 molar; 25ml.). The reaction mixture was heated under reflux for 1 hr., and worked up as in (a) above to give (245) (1.68gm. - 87%), with properties identical to those reported in (a) above.

Preparation of undecane-2,7-dione(237).

A solution of (246) (330mg.) in aqueous methanol (85%; 10ml.), containing one drop of concentrated hydrochloric acid, was heated on a steam bath for 30 min. After cooling, the methanol was removed under reduced pressure, and the residue was extracted with ether. The ethereal extract was washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave undecane-2,7-dione(237) (280mg. - 89%) as plates, m.p. 39.5-40° from petrol. (Dobson[217] gives m.p. 41°). The overall yield from cyclohexanone was 14%. The mass spectrum showed a molecular ion at 184, ($C_{11}H_{20}O_2$ requires M.W. 184) and t.l.c. (alumina - 5% benzene - petrol as eluent, R_F 0.4; silica - 25% chloroform - benzene as eluent, R_F 0.8; silica - chloroform as eluent, R_F 0.7) showed only one spot. G.l.c. data (see g.l.c. experimental) always showed only one peak. The i.r. spectrum (CCl_4 solution) showed absorption at 1715cm.$^{-1}$, and (melted film) absorption at 1706, 1467, 1420, 1414, 1373 and 1358cm.$^{-1}$.

Preparation of 2,2,7,7-bisethylenedioxyundecane(247).

Undecane-2,7-dione(237) (5mg.), ethylene glycol (0.15ml.), p-toluenesulphonic acid (5mg.) and ethyl orthoformate (0.3ml.) were heated to 160-170°, and the more volatile liquids allowed to distil off. The residue was dissolved in chloroform (5ml.) and used directly for g.l.c. investigation.

Preparation of 2-n-butyrylcyclohexanone(249)[217].

Cyclohexanone(240) (7.8gm.), n-butyric anhydride (25.3gm.) and boron trifluoride - acetic acid (1:1) complex (54.4gm.) were mixed with external cooling (ice-bath) and stirring. After 30 min., the stirring was stopped, the ice-bath removed and the reaction mixture allowed to stand for 4 hr., when it was poured into aqueous sodium acetate solution (containing 26.2gm.) and heated under reflux for 1 hr. After cooling, the reaction mixture was extracted with petrol. The extracts were washed with aqueous sodium bicarbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent and distillation of the residual oil gave 2-n-butyrylcyclohexanone(249) (7.22gm. - 54%) as a clear mobile oil, b.p. 128-130° /15mm. (Adams and Hauser[232] give b.p. 133-134°/20mm.). The compound gave a deep purple coloration with ferric chloride in methanol (characteristic of β-diketones etc.) and the i.r. spectrum (liquid film) showed two peaks in the carbonyl region at ~1700cm.$^{-1}$ and ~1600cm.$^{-1}$, again

a characteristic feature of a β-diketone.

Preparation of 7-ketodecanoic acid(250)[217].

2-n-Butyrylcyclohexanone(249) (22.3gm.) was heated under reflux for 2 hr. in aqueous sodium hydroxide solution (6.7gm. in 125ml.). After cooling, and extraction with ether, the alkaline extract was acidified with dilute hydrochloric acid and extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave (250) as a low melting solid (18.5gm. - 75%) which was purified by distillation, b.p. 144-149°/0.3mm., and recrystallisation from petrol, to give plates, m.p. 42-43°. (Manyik, Frostick, Sanderson and Hauser[223] give b.p. 157-158°/2.5mm., m.p. 42-43°). (Found: C, 64.35; H, 9.90. $C_{10}H_{18}O_3$ requires C, 64.50; H, 9.75%). T.l.c. (silica - chloroform as eluent) showed only one tailing spot, $R_F \sim 0.1$. The i.r. absorption data (Table 12) confirm that the compound is a keto-acid.

Preparation of 2-hydroxyethyl 7,7-ethylenedioxydecanoate(251).

The ester (251) was prepared from 7-ketodecanoic acid(250) (7.44gm.), ethylene glycol (24.8gm. - 0.4 mole) and p-toluene-sulphonic acid (12.mg.) in anhydrous benzene (175ml.), as in the previous preparation of (248). The ester (251) was obtained (9.98gm. - 91%) as a clear viscous oil which could not be distilled.

T.l.c. (silica - chloroform as eluent) showed one spot, R_F 0.55, and the i.r. spectrum (CCl_4 solution) showed typical ester absorption at 1742cm.$^{-1}$ (Table 12).

Preparation of lithium 7,7-ethylenedioxydecanoate(252).

This lithium salt (252) was prepared in the same way as (243) from 2-hydroxyethyl 7,7-ethylenedioxydecanoate(251) (9.98gm.) in aqueous lithium hydroxide solution, (0.96gm. in 100ml.). The salt (252) was obtained as a white solid (7.4gm. - 86%), which did not melt below 350°.

Preparation of 8,8-ethylenedioxyundecan-2-one(253).

This ketone (253) was prepared from a suspension of the lithium salt (252) (7.4gm.) in dry ether (25ml.) and ethereal methyllithium (1.81 molar; 100ml.), in the same way as (245). The ketone (253) was obtained as a clear viscous oil, (5.8gm. - 81%) b.p. 103-105°/10^{-2}mm., n_D^{25} 1.4551. (Dobson [217] gives b.p. 110-112°/10^{-2}mm., n_D^{25} 1.4552). T.l.c. (silica - chloroform as eluent) gave one spot, R_F 0.8. The i.r. spectrum (CCl_4 solution) showed ketonic carbonyl absorption at 1721cm.$^{-1}$.

Preparation of undecane-2,8-dione(238).

The ketone (253) (1.3gm.) was hydrolysed exactly as in the cognate preparation of (237) above, to give undecane-2,8-dione(238)

(1.91gm. - 87%), which crystallised from petrol as plates m.p. 36-38°. (Dobson[217] gives m.p. 41°). The overall yield from cyclohexanone was 23%. The mass spectrum (probe) showed a molecular ion at 184, ($C_{11}H_{20}O_2$ requires M.W. 184), whereas the mass spectrum using the "hot tank" technique showed a molecular ion at 136, 18 mass units less than the molecular weight required. This spectrum can be interpreted (due to the large 124 peak) on the basis of a cyclic structure (259), formed in the hot tank from (238), via an internal aldol condensation, followed by dehydration. T.l.c. (alumina - 50% benzene - petrol as eluent, R_F 0.4; silica - 25% chloroform - benzene as eluent, R_F 0.2; silica - chloroform as eluent, R_F 0.7) showed only one spot. G.l.c. data (see g.l.c. experimental) always showed only one peak. The i.r. spectrum (CCl_4 solution) showed absorption a 1722cm.$^{-1}$, and (melted film) absorption at 1715, 1467, 1415 and 1363cm.$^{-1}$.

Preparation of 2,2,8,8-bisethylenedioxyundecane(254).

The bis-ketal (254) was prepared for g.l.c. investigation in exactly the same way as (247), from undecane-2,8-dione(238) (50mg.).

Preparation of 2-hydroxyethyl stearate(260).

Stearic acid (1gm.) and ethylene glycol (3ml.) were heated under reflux for 2 hr. in benzene (25ml.) containing concentrated sulphuric acid (2 drops). On cooling, solid sodium carbonate was

added, and the reaction mixture shaken thoroughly. Water was added, and the benzene layer separated. The benzene solution was extracted with aqueous sodium hydrogen carbonate solution, washed with water, dried (magnesium sulphate) and filtered. Evaporation of the benzene gave (230) (950mg. - 82%) as plates, m.p. 52° from petrol. T.l.c. (silica - 10% ethyl acetate - petrol as eluent) showed only one spot, R_F 0.2, and the i.r. spectrum (CCl_4 solution) showed typical ester absorption at 1743cm.$^{-1}$ and hydroxyl absorption at 3624cm.$^{-1}$ and 3520cm.$^{-1}$, (Table 12).

Hydration of octa-1,7-diyne(60) and undeca -1,7-diyne(236).

(a) Mercuric sulphate-sulphuric acid method[189-191,220].

(i) Octa-1,7-diyne(60) (108mg.), mercuric sulphate (10mg.) and concentrated sulphuric acid (10mg.) were heated under reflux for 6 hr. in aqueous ethanol (75%; 3ml.). After cooling, aqueous sodium hydrogen carbonate solution was added to neutralise the sulphuric acid, and the reaction mixture extracted with ether. The ethereal extract was washed with water, dried (magnesium sulphate) and filtered. Evaporation of the ether gave octane-2,7-dione(239) (78mg. - 61%), plates, m.p. 41-42° from petrol. (Hückel and Wörffel[233] give m.p. 43°). The mass spectrum showed a molecular ion at 142, ($C_8H_{14}O_2$ requires M.W. 142). T.l.c. (silica - chloroform as eluent) showed only one spot, R_F 0.75. The i.r. spectrum (melted film) showed typical carbonyl absorption

at ~1720cm.$^{-1}$.

(ii) Undeca-1,7-diyne(236) (137mg.) was treated exactly as above. Removal of the solvent gave a low-melting (~25°) crystalline solid (137mg.). The i.r. spectrum (melted film) was devoid of absorption at ~3300cm.$^{-1}$ (ν≡C-H), and showed absorption at ~1720cm.$^{-1}$ (νC=O). T.l.c. (silica - chloroform as eluent) showed a spot of R_F 0.7. This crude solid was dissolved in chloroform (5ml.) and analysed directly by g.l.c. (see Discussion).

(b) Mercuric oxide - boron trifluoride method[218].

(i) Octa-1,7-diyne(60) (95mg.), mercuric oxide (12.5mg.), boron trfluoride - ether complex (6μl.) and trichloroacetic acid (1mg.), were stirred in methanol (5ml.) for 24 hr. The reaction mixture was poured into dilute sulphuric acid and shaken well. After ether extraction, the ether layer was washed with aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the ether gave a crystalline low-melting solid (59mg.), whose i.r. spectrum (melted film), and t.l.c. behaviour were virtually identical to those of the crude solid obtained in (a) (i) above.

(ii) Undeca-1,7-diyne(236) (118mg.) was treated exactly as above and gave a crystalline, low-melting solid (149mg.), whose i.r. spectrum (melted film) and t.l.c. behaviour were virtually identical to those of the crude solid obtained in (a) (ii) above. The crude solid was dissolved in chloroform (5ml.) and analysed

directly by g.l.c. (see Discussion).

(c) Mercuric chloride - aniline method[219].

(i) Octa-1,7-diyne(60) (85mg.) in benzene (13ml.) was added to a mixture of mercuric chloride (915mg.) in water (1ml.) and aniline (168mg.) in benzene (18ml.), and the reaction mixture stirred at 50° for 18 hr. After cooling, hydrochloric acid (36%; 1ml.) was added, and the reaction mixture saturated with hydrogen sulphide and filtered. The black precipitate was washed with benzene, and the combined benzene extract and washings were washed successively with aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the benzene gave a brown oil (53mg.), whose i.r. spectrum (liquid film) showed absorption at ~1710cm.$^{-1}$ (νC=O), but no absorption at ~3300cm.$^{-1}$ ($\nu\equiv$C-H). T.l.c. (silica - chloroform as eluent) showed a large spot, R_F 0.75, plus several indistinct spots.

(ii) Undeca-1,7-diyne(236) (127mg.) was treated exactly as above, and gave a brown oil (107mg.). The i.r. spectrum (liquid film) was very similar to that of the crude solid obtained in (a) (ii) above, but t.l.c. showed, in addition to the main spot, R_F 0.7, two other less distinct spots, R_F 0.8 and 0.85. The oil was dissolved in chloroform (5ml.) and analysed by g.l.c. as before, (see Discussion). Two other peaks, retention times 22 min. and 32 min., were observed in addition to the peaks corresponding to the two ketones, (237) and (238).

(d) Mercury-impregnated resin method[225].

(i) Octa-1,7-diyne(30) (141mg.) and mercury-impregnated amberlite [IR-120, (11)] resin (129mg.) were heated under reflux in aqueous acetic acid (10%; 10ml.) for 3 hr., during which time the brown resin turned black. After cooling and filtering, concentrated aqueous sodium hydroxide solution was added to neutralise the acetic acid, and the reaction mixture extracted with ether. The ethereal extract was washed thoroughly with water, dried (magnesium sulphate) and filtered. Removal of the ether gave a brown oil (75mg.). The i.r. spectrum (liquid film) showed a small peak at ~3300cm.$^{-1}$ ($\nu\equiv$C-H) and a large peak at ~1720cm.$^{-1}$ (νC=O). T.l.c. (silica - chloroform as eluent) showed essentially only one spot, R_F 0.75.

(ii) Undeca-1,7-diyne(236) (110mg.) was treated exactly as above, and gave a brown oil (94mg.), whose i.r. spectrum (liquid film) showed a small peak at ~3300cm.$^{-1}$ ($\nu\equiv$C-H), and strong absorption at ~1710cm.$^{-1}$ (νC=O). T.l.c. (silica - chloroform as eluent) showed mainly a spot of R_F 0.7, plus several other indistinct spots. The oil was dissolved in chloroform (5ml.) and analysed by g.l.c. as before (see Discussion). In addition to the two main peaks, several other peaks were observed in the g.l.c. traces.

(iii) In order to account for several unexpected peaks in the g.l.c. traces, a blank reaction was carried out on the resin (150mg.) as before. Analysis of this blank run showed several

peaks on g.l.c., confirming the idea that the extra peaks in the g.l.c. traces of the solution described in (d) (ii) above, were probably due to low-boiling material which had been extracted from the resin.

Reaction of octa-1,7-diyne(60) with aqueous ruthenium trichloride in hydrochloric acid.

Octa-1,7-diyne(60) (117mg.) was stirred at 50° in an aqueous solution (5ml.) of ruthenium trichloride trihydrate (0.1 molar) and hydrochloric acid (5 molar), for 20 hr. After cooling, the reaction mixture was extracted with ether, washed thoroughly with water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave a brown oil (94mg.), whose i.r. spectrum (liquid film) showed absorption at ~3300cm.$^{-1}$, ~2100cm.$^{-1}$, ~2050cm.$^{-1}$, ~1980cm.$^{-1}$, ~1710cm.$^{-1}$, ~1650cm.$^{-1}$ and ~1600cm.$^{-1}$. The absorption at ~2050cm.$^{-1}$ and ~1980cm.$^{-1}$ was very strong.

Reaction of phenylacetylene(77) with aqueous ruthenium trichloride in hydrochloric acid.

Phenylacetylene(77) (96mg.) (ethynyl content[186] 0.98 active hydrogens per mole) was treated as above and gave an oil, (108mg. - 93%), identified as acetophenone by comparison of its i.r. spectrum with that of an authentic sample, when they were shown to be identical, and characterised as the 2,4-dinitrophenylhydrazone

derivative, needles m.p. 236-237° from acetic acid. The m.p. of an authentic sample of acetophenone 2,4-dinitrophenylhydrazone was 237° (from acetic acid), and the mixed m.p. was 236-237°.

Reaction of oct-1-yne(217) with aqueous ruthenium trichloride in hydrochloric acid.

Oct-1-yne(217) (100mg.) (ethynyl content[186] 0.99 active hydrogens per mole) was treated as in the previous reaction of (60). Evaporation of the solvent gave an oil (74mg.) whose i.r. spectrum (liquid film) showed absorption at ~3300cm.$^{-1}$, ~2130cm.$^{-1}$, ~2070cm.$^{-1}$, ~1980cm.$^{-1}$, ~1720cm.$^{-1}$ and ~1620cm.$^{-1}$. G.l.c. analysis [25% Apiezon "L" grease on Celite, (80-100 mesh), at 75°] showed five peaks, retention times 2.2 min. (~5%), 2.9 min. (~5%), 6.7 min. (~20%), 23.8 min. (~40%) and 27.2 min. (~30%). The peak of retention time 6.7 min. was shown to be due to unchanged (217) and the peak of retention time 23.8 min. was shown to be due to octan-2-one (255). Washing the solution with aqueous silver nitrate removed the peak of retention time 6.7 min., showing that this peak was not due to a rearrangement taking place on the column.

Reaction of oct-1-yne(217) with hydrochloric acid.

Oct-1-yne(217) (100mg.) in hydrochloric acid (5 molar; 5ml.) was stirred at 50° for 24 hr. The reaction mixture was worked up as before, and gave an oil (63mg.) whose i.r. spectrum (liquid film)

was virtually identical to that of oct-1-yne, except for a small peak at ~1720cm.$^{-1}$. G.l.c. analysis as before showed only two peaks, retention times 6.7 min. (~95%), due to oct-1-yne(217), and 23.8 min. (~5%), due to octan-2-one(255).

Reaction of oct-1-yne(217) with aqueous ruthenium trichloride.

Oct-1-yne(217) (100mg.) was stirred at 50° for 24 hr. in aqueous ruthenium trichloride solution (0.1 molar; 5ml.). The reaction mixture was worked up as before, and evaporation of the ether gave an oil (69mg.), whose i.r. spectrum (liquid film) showed absorption at ~3300cm.$^{-1}$, ~2130cm.$^{-1}$ and ~1720cm.$^{-1}$. G.l.c. analysis as before showed two peaks, retention times 6.7 min. (~65%), due to oct-1-yne(217), and 23.8 min. (~35%), due to octan-2-one(255).

Reaction of oct-1-yne(217) with ethereal ruthenium trichloride.

Oct-1-yne(217) (100mg.) in a solution of trichloride trihydrate in ether (0.1 molar; 5ml.) was stirred and heated under reflux for 24 hr. Work up in the usual way gave an oil (72mg.), whose i.r. spectrum (liquid film) showed slight absorption at ~3300cm.$^{-1}$ and ~2130cm.$^{-1}$, and strong absorption at ~1720cm.$^{-1}$. G.l.c. analysis as before showed two peaks, retention times 6.7 min. (~20%), due to oct-1-yne(217), and 23.8 min. (~80%), due to octan-2-one(255).

Reaction of oct-1-yne(217) with ruthenium trichloride trihydrate in ether, saturated with gaseous hydrogen chloride.

Ether was saturated with dry hydrogen chloride, and ruthenium trichloride was added, to make a solution of 0.1 molar concentration. Oct-1-yne(217) (100mg.) was added to this solution (5ml.) and the reaction mixture was stirred and heated under reflux for 4 hr. The reaction mixture was worked up as before, and gave an oil (110mg.) whose i.r. spectrum (liquid film) showed absorption at ~1720cm.$^{-1}$. G.l.c. analysis as before, showed that the oil was mainly octan-2-one(255) (~95%).

Reaction of oct-1-yne(217) with anhydrous ruthenium trichloride in ether, saturated with gaseous hydrogen chloride.

Anhydrous ether was saturated with anhydrous hydrogen chloride, and anhydrous ruthenium trichloride (prepared by heating powdered ruthenium trichloride trihydrate at 130°) was added to this solution (5ml.) to make a solution of 0.1 molar concentration. (Note that the anhydrous ruthenium trichloride was not very soluble in ether). Oct-1-yne(217) (100mg.) was added, and the reaction mixture stirred and heated under reflux for 4 hr. Work up in the usual manner gave unchanged oct-1-yne(217) (71mg.), identical to the starting material by i.r. and g.l.c.

Preparation of octan-2-one(255).

A solution of octan-2-ol(256) (2.5gm.) in acetone (15ml.) was oxidised using excess of Jones reagent[234], (8N chromium trioxide in concentrated sulphuric acid). The reaction mixture was poured into water and extracted with ether. The ether extract was washed with water, aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the solvent gave octan-2-one(255) (2.1gm. - 85%) as an oil, b.p. 173°, n_D^{21} 1.4150. (Verhulst and Glorieux[235] give b.p. 173°, n_D^{20} 1.4151). The 2,4-dinitrophenylhydrazone derivative was obtained as orange needles, m.p. 57.5-58° from ethanol (Moureu and Mignonac[236] give m.p. 58°). (Found: C, 54.20; H, 6.65; N, 18.40. $C_{14}H_{20}N_4O_4$ requires C, 54.50; H, 6.55; N, 18.20%). The i.r. spectrum (liquid film) of octan-2-one(255) showed absorption at ~1720cm.$^{-1}$ (νC=O) and t.l.c. (silica - 10% ethyl acetate as eluent) showed one spot, R_F 0.55. G.l.c. [25% Apiezon "L" grease on Celite (80-100 mesh) at 75°] showed only one peak, retention time 23.8 min.

Attempted preparation of 2-chlorooct-1-ene(257).

A mixture of oct-1-yne(217) (4.5gm.), cuprous chloride (1gm.), ammonium chloride (450mg.), pyrogallol (25mg.) and concentrated hydrochloric acid (7ml.) was stirred at room temperature for 6 hr. Ether was added, and the reaction mixture shaken thoroughly. The

ether layer was washed with water, aqueous sodium hydrogen carbonate solution and water, dried (magnesium sulphate) and filtered. Evaporation of the ether and distillation gave unchanged oct-1-yne(217) (4gm.) and octan-2-one(255) (200mg.), identified as before by i.r. and g.l.c.

G.l.c. experimental.

The g.l.c. separation of the two isomeric diketones (237) and (238) was attempted first on a Pye Argon Chromatograph using 43" x 1/5" columns packed as given below with the conditions:-

(i) 10% Apiezon "L" grease on Celite (80-100 mesh) at 140°.
(Retention time of both diketones, 1 hr. 35 min.).

(ii) 1% polyethyleneglycol adipate on Embacel at 100°.
(Retention time of both diketones, 17 min.).

(iii) 10% polyethyleneglycol adipate on Embacel at 140°.
(Retention time of both diketones, 47 min.).

(iv) 1% S.E.30 on Embacel at 75° and 50°.
(Retention times of both diketones, 19 min. and 1 hr. 10 min., respectively).

(v) 1% Q.F.I. on Embacel at 75°.
(Retention time of both diketones, 1 hr. 15 min.).

(vi) 5% Carbowax 400 on Embacel at 125°.
(Retention time of both diketones, 30 min.).

(vii) 5% Carbowax 600 on Embacel at 125°.
(Retention time of both diketones, 35 min.).

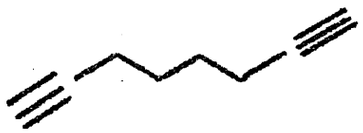
(viii) 25% Carbowax on Embacel at 125°.
(Retention time of both diketones, 2 hr. 10 min.).

The bis-ketals of both diketones (247) and (254), on a column of 0.5% Apiezon "L" grease on Celite (80-100 mesh) at 100°, had retention times of 1 hr. 14 min. and 1 hr. 17 min., for (247) and (254), respectively, but this separation was only partial, and was

not good enough for quantitative estimation of the peaks.

Separation of the diketones (237) and (238) was achieved using a Perkin-Elmer 451 Fractometer, with a 50 metre Golay capillary column coated with polypropylene glycol. The temperature was 150°, the flow rate 55ml./min. of helium and the splitting ratio 2:1::column:vent. Under these conditions, the retention time of (237) was 35½ min., that of (238) being 37 min. The column resolution[237] was 1.57, and the column efficiency[238] was 577. Equimolar mixtures of the diketones separated sufficiently well to enable quantitative area measurements to be made, but it was found, rather surprisingly, that the flame-ionisation detector was about 2½ times more sensitive to the 2,7-isomer (237) than to the 2,8-isomer (238). This unusual result was checked and rechecked, but there appears to be no doubt as to its validity.

Known mixtures of the two diketones were made up in solution in chloroform, and analysed by g.l.c. (sample size ~10μl of a 0.5% solution). The areas of the peaks were measured by triangulation and square counting. A plot of area ratio to weight ratio was drawn, and produced, as expected, a straight line passing through the origin. The hydration products in chloroform were then analysed under the same conditions, and the peaks were measured (square counting). Using the graph above, the ratio of (237) to (238) by weight was obtained. In all cases, the ratio of the 2,7-diketone (237) to the 2,8-diketone (238) was approximately 2 : 1 (Table 13).



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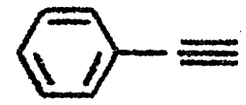

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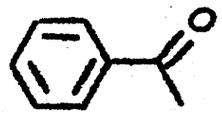

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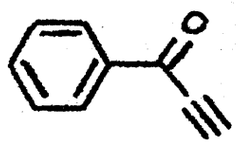

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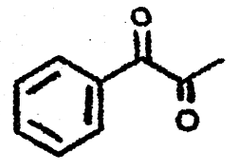

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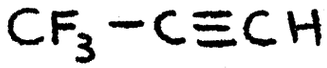

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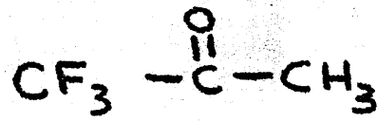

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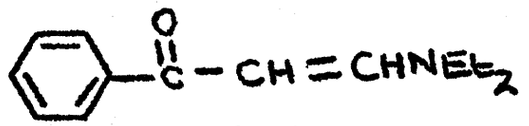

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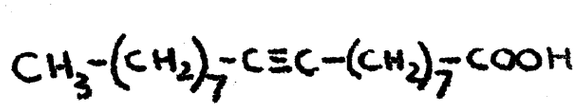

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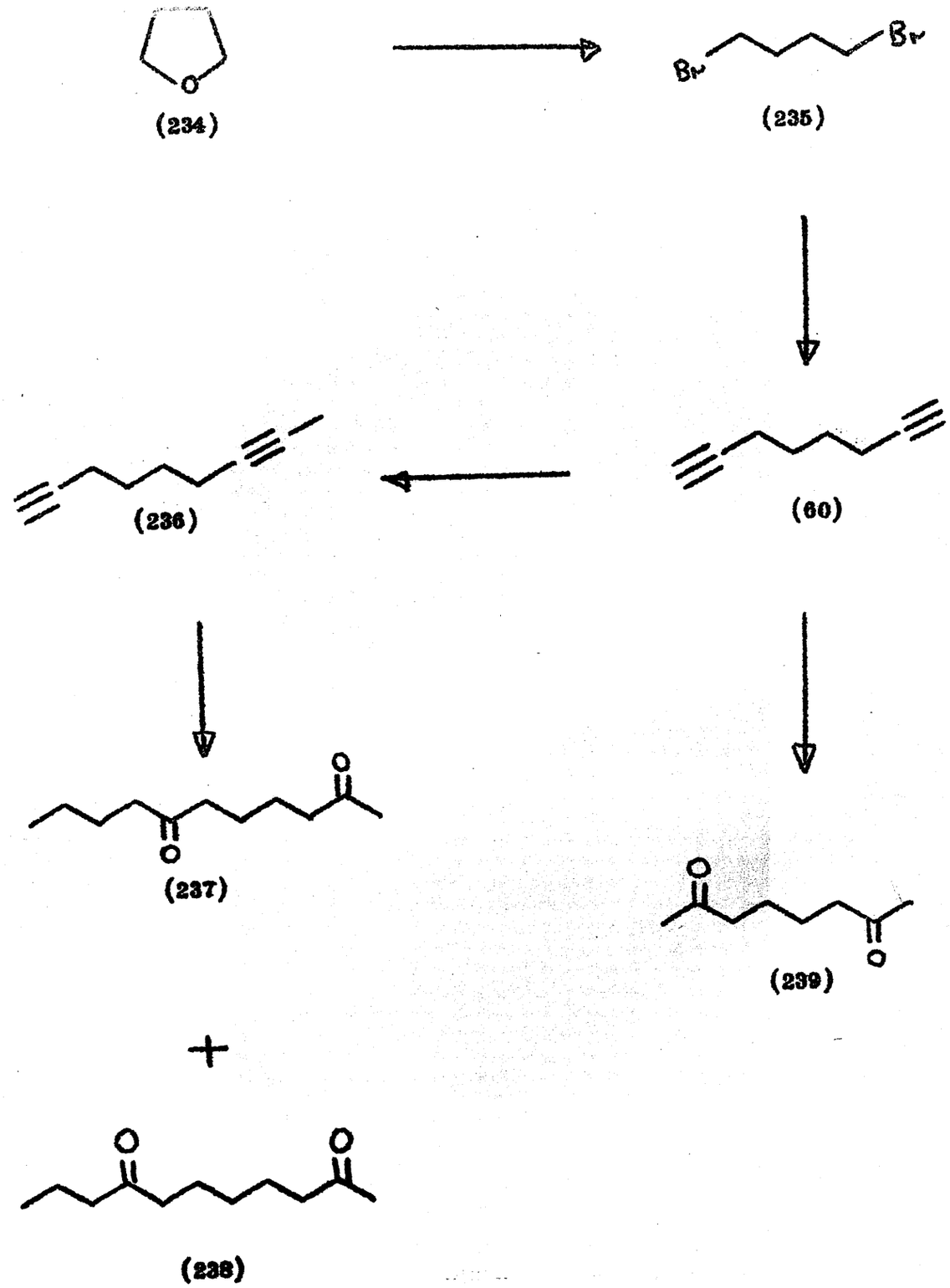
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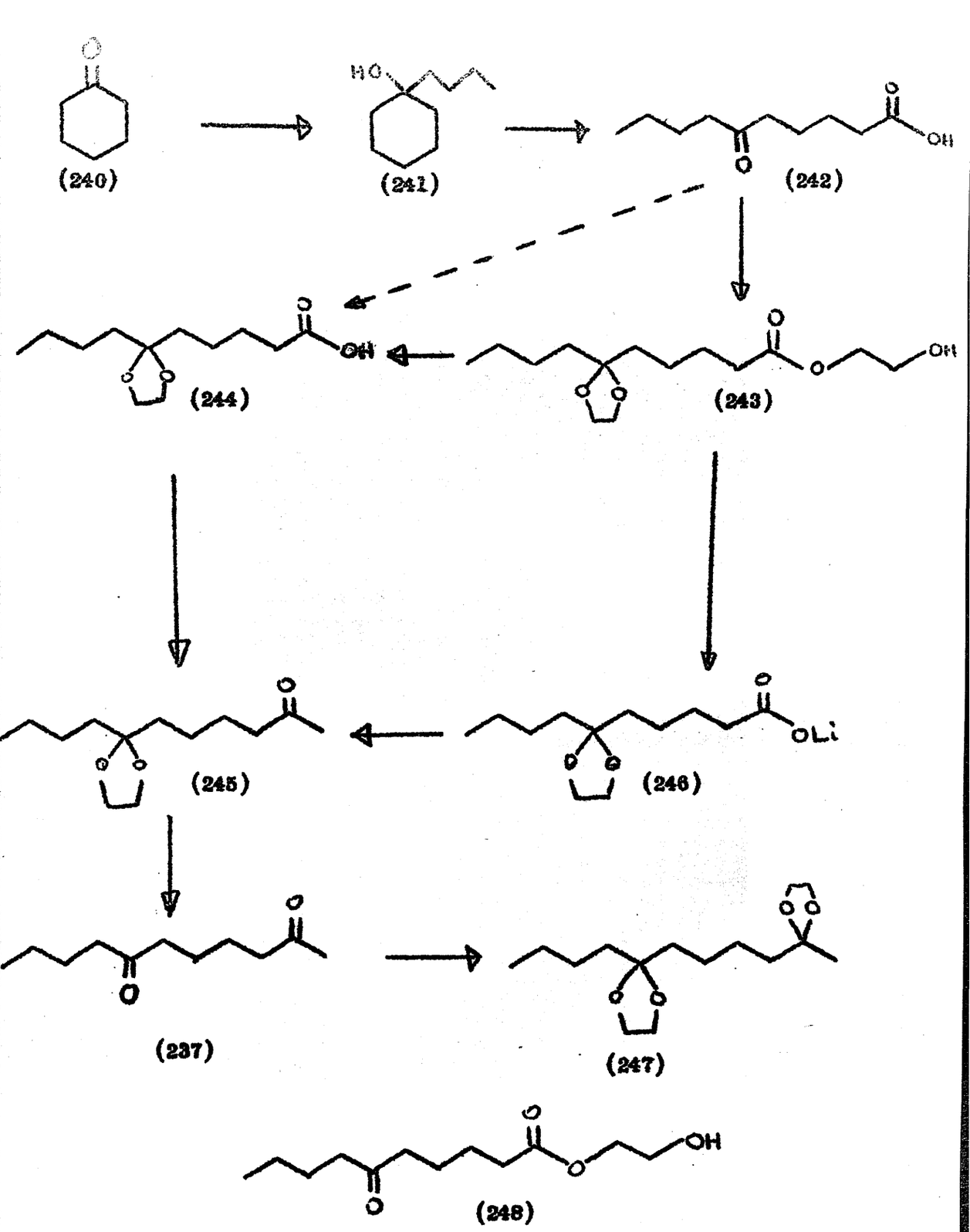
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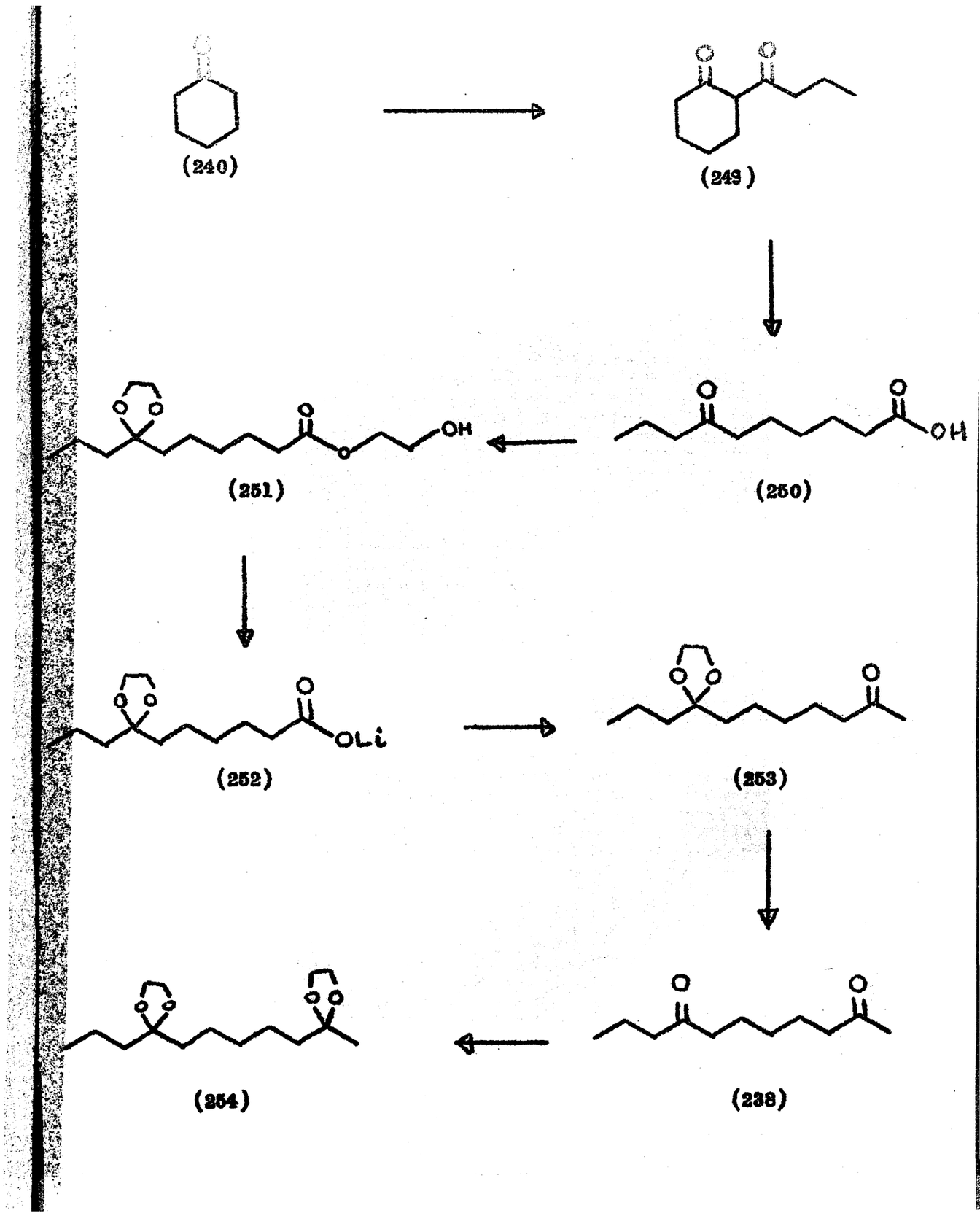
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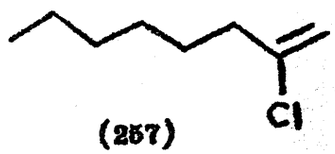

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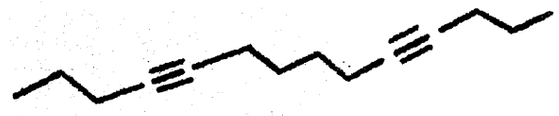

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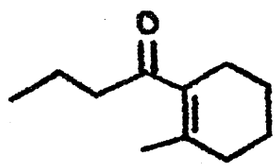

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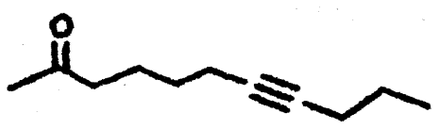

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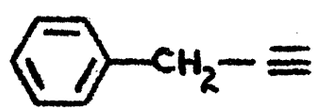

(262)

TABLE 12 - CARBONYL AND HYDROXYL STRETCHING ABSORPTIONS IN SOLUTION.

Compound	Solvent	Molarity	Cell length (cm.)	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε	ν(cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}$(cm.$^{-1}$)	ε
CARBONYL ABSORPTIONS												
Undecan-4-one	CCl_4	0.022	0.051	1716[a]	18	320						
Undecan-4-one	Et_2O/CCl_4*	0.023	0.051	1716[a]	18	310						
Stearic acid	CCl_4	0.0014	0.5	1759[b]	23	175	1711[c]	15	605			
Stearic acid	CCl_4	0.00035	2	1759[b]	23	285	1711[c]	15	400			
Stearic acid	Et_2O/CCl_4*	0.0028	0.2	1737[d]	22	480						
6-Ketodecanoic acid	n-hexane	0.0073	0.051	1766[b]	22	85	1715[e]	18	900			
6-Ketodecanoic acid	CCl_4	0.0021	0.5	1759[b]	23	155	1713[e]	19	790			
6-Ketodecanoic acid	CCl_4	0.00063	0.5	1759[b]	23	230	1713[e]	19	685			
6-Ketodecanoic acid	$CHCl_3$	0.0024	0.2	1748[d]	35	295	1710[e]	21	520			
6-Ketodecanoic acid	Et_2O/CCl_4*	0.0028	0.2	1736[d]	26	465	1718[a]	22	405			
7-Ketodecanoic acid	Et_2O/CCl_4*	0.0031	0.2	1738[d]	26	470	1720[a]	21	415			
2-Hydroxyethyl stearate	CCl_4	0.0013	0.5	1743[f]	25	425						
2-Hydroxyethyl stearate	Et_2O/CCl_4*	0.013	0.051	1743[f]	25	485						
2-Hydroxyethyl 6,6-ethylene-dioxydecanoate	CCl_4	0.0023	0.5	1741[f]	26	435						
2-Hydroxyethyl 6,6-ethylene-dioxydecanoate	Et_2O/CCl_4*	0.0019	0.5	1741[f]	26	485						
2-Hydroxyethyl 7,7-ethylene-dioxydecanoate	CCl_4	0.0021	0.5	1742[f]	25	475						
6,6-Ethylenedioxydecanoic acid	Et_2O/CCl_4*	0.0029	0.2	1737[d]	25	475						
Attempted ketalisation of (242)	CCl_4	0.0019	0.5	1759[b]	—	140	1742[g]	26	315	1714[e]	22	410
Attempted ketalisation of (242)	Et_2O/CCl_4*	0.0026	0.2	1739[h]	22	485	1719[a]	22	315			
HYDROXYL ABSORPTIONS												
Stearic acid	CCl_4	0.00035	2	3535	24	50						
Stearic acid	Et_2O/CCl_4*	0.0028	0.2	~3500	—	30	~3150[i]	—	90			
6-Ketodecanoic acid	CCl_4	0.0021	0.2	3534	25	45						
6-Ketodecanoic acid	CCl_4	0.00063	2	3534	25	70						
6-Ketodecanoic acid	Et_2O/CCl_4*	0.0028	0.2	~3500	—	30	~3140[i]	—	85			
2-Hydroxyethyl stearate	CCl_4	0.0016	2	3624	—	50	3520[j]	—	15			
2-Hydroxyethyl stearate	Et_2O/CCl_4*	0.016	0.2	3624	—	15	3470[i]	—	100			
2-Hydroxyethyl 6,6-ethylene-dioxydecanoate	CCl_4	0.0023	2	3642	—	20	3623	—	40	3536[j]	—	70
Attempted ketalisation of (242)	CCl_4	0.0019	2	3640	—	15	3623	40	25	3536[j]	39	50

* 1 : 4, by volume

Assignments:-

[a] νCO ketone.
[b] νCO acid monomer.
[c] νCO acid dimer.
[d] νCO acid monomer bonded to ether.
[e] νCO acid dimer and ketone.
[f] νCO ester.
[g] νCO acid monomer and ester.
[h] νCO ester and acid monomer bonded to ether.
[i] νOH inter-bonded to ether.
[j] νOH intra-bonded to ester carbonyl.

TABLE 13 - PROPORTION OF (237) AND (238) OBTAINED FROM HYDRATION OF (236).

Hydration reagent	%(238)	%(237)
BF_3 - HgO	31	69
$HgSO_4$ - H_2SO_4	31	69
$HgCl_2$ - aniline	34	66
Hg-resin*	24	76

* Too much trust cannot be placed in the results obtained with the mercury resin, since extra peaks in the g.l.c. traces confuse the issue, and blank runs are not reproducible.

TABLE 14 - REACTIONS OF OCT-1-YNE(217).

Reagent	Products	Comments
HCl	(255; 5%), (217; 95%)	No "allene" (i.r. and g.l.c.)
$RuCl_3$/ether	(255; 80%), (217; 20%)	No "allene" (i.r. and g.l.c.)
$RuCl_3$/water	(255; 35%), (217; 65%)	No "allene" (i.r. and g.l.c.)
$RuCl_3$/ether/HCl gas	(255; 95%)	No "allene (i.r. and g.l.c.), and shorter reaction time than reported method[201].
Anhydrous $RuCl_3$/ether/HCl gas	(217; 70%)	No "allene (i.r. and g.l.c.)

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